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THERMOLUMINESCENCE PARAMETERS OF QUARTZ EXTRACTED FROM BEACH SAND

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Abstract: In this work, the dosimetric characteristics and kinetic parameters of sand samples from a beach on the Caspian Sea coast of eastern Baku were investigated using the TL technique. The TL glow curve of the natural, unheated quartz deconvoluted using the GlowFit program. It was found that, at least three peaks located at 260ºC, 318ºC, 366ºC which corresponds to the electron traps with the depth of 0.96, 0.97 and 1.2 eV respectively. Calculated frequency factor values related to those centers are within the acceptable range and correlates with the figures reported earlier for the variety of sand samples. The glow curves of preheated sand samples exhibit four poorly resolved peaks due to the overlapping of individual peaks at low and high temperature zones. The deconvolution of those glow curves enables us to separate at least five peaks with the T_{max} close to the reported earlier in the literature.

Keywords: quartz; deconvolution; thermoluminescence

Thermo-stimulated luminescence (TL) of the natural crystals widely used for the estimation of the ages some of the archeological artifacts such as pottery, furnace, baked bricks, tiles, etc. Quartz inclusions are part of the composition of porcelain goods and “quartz inclusion technique” conventionally used for the TL dating of ancient pottery artifacts. The method based on the separation of quartz from the pottery and determination of radiation dose that quartz inclusions received from the surrounding environment since it has been fired when it was manufactured. Initial heating sets to zero the TL sensitivity of the quartz inclusions of pottery materials at temperatures more than 500ºC which is the usual temperature for the pottery manufacturing. This event happens when quartz or other crystals exposed to open sunlight as well and known as “bleaching”. Further irradiation leads to the accumulation of the TL centers which are proportional to the absorbed dose.

The origin of quartz inclusions comes from either row clay which has been manufactured the pottery or added during the process to improve/change the quality of the pottery goods. Therefore, the TL investigation of quartz crystals has been applied for dating [1]–[3] and dosimetric purposes [4].

The TL characteristics of quartz crystals highly depend on their origin and thermal treatment [5] due to defects in a crystal lattice or impurity atoms like Al or Ti. Therefore, it should be anticipated that the TL parameters of quartz inclusions extracted from different archeological artifacts would depend on the prehistory of its production.

TL spectrum of the quartz is complex and consists of several individual peaks [2], [6]–[10]. The analysis of thermoluminescence data includes, but not limited, the separation of a glow curve into separate glow peaks. This technique is especially useful if different experimental conditions are to be studied. For the last 30 years, a variety of glow curve analysis methods have been applied extensively using special computer programs, known as computerized glow curve deconvolution or computerized glow curve analysis (GCA). At the beginning pure and modified Gaussian expressions were used for fitting glow peaks, but the glow peak functions proposed by

Kitis et al. [11] much increased the accuracy of GCA programs by providing simple functions for first-order, second-order, and general-order kinetics.

The aim of the work is to investigate the TL parameters of both natural and preheated sand samples with the use of GCA.

1. Materials and methods

As a sample, we have taken the sand from a beach on the Caspian Sea coast of eastern Baku. Sand samples were sieved and the fraction of 100-160 µm of sand 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. Irradiation was performed at ambient temperature with a ^{60}Co gamma source with a dose rate of 37.3 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).

The Harshaw TLD 3500 Manual Reader is used to measure the characteristics of TL samples. TL measurements were performed using a linear heating rate 20^{o}C/s from 50^{o}C to 400^{o}C. 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 sand grains was laid on the planchet surface in order to get full contact that ensures uniform TL signal from the sand.

The quality of the fit produced by the fitting equation to experimental glow curve i.e. ‘‘goodness of fit’’ is judged using the figure of merit (FOM) approach. The FOM in percent is defined as

$$FOM(\%) = \sum_{Tstart}^{Tstop} \frac{|y_T - \quad y(x_T)|}{A}$$

where T_{start} is initial temperature in the fit region, T_{stop} is the ending temperature in the fit region, y_T is the photomultiplier tube (PMT) current at temperature T, $y(x_T)$ is the value of the fit function at x_T, and A is the area under the peak, i.e., the integral of the fit function between T_{start} and T_{stop}

2. Results and Discussions

A computerized glow curve fitting procedure has been applied for the experimental glow curve of unheated natural (not irradiated at the laboratory) sand sample by assuming first order kinetic model Randall and Wilkins. The GlowFit program is used to find the best possible fit to the experimental data. Glow fit program designed for the analysis of TL glow curve based on first order kinetic model and able to calculate major trapping parameters. A fitting equation describing a glow peak using first-order kinetics was deduced by Kitis et al. [11] as

$$I(T) = \mathrm{I_m} \exp\{1 + \frac{\mathrm{E(T - T_m)}}{\mathrm{kT \cdot T_m}} - \frac{\mathrm{T^2}}{\mathrm{T_m^2}} \cdot \exp\left(\frac{\mathrm{E(T - T_m)}}{\mathrm{kT \cdot T_m}}\right)(1 - \Delta) - \Delta_\mathrm{m}\}$$

where I(T) is the peak intensity I at temperature T in K, I_m is the intensity at the peak maximum, E is the activation energy in eV, k is the Boltzmann constant in eV K^{-1}, T_m is the temperature at the peak maximum in K, Δ is $2kT(E)^{-1}$, and Δ_m is $2kT_m(E)^{-1}$. The GCA program fits the glow curve data to a sum of functions similar to Eq. (1), hwith different terms E, T, Tm, and Im for each peak, using a least-squares method for non-linear functions and the Levenberg–Marquardt algorithm for minimization.

The main parameters of the trapped electrons and holes are the activation energy, the escape frequency factor, and the recombination and re-trapping probability coefficients. These parameters and the relation between them are of importance in determining the temperatures of the TL peaks, their dose dependence as well as other properties, in particular, their stability at ambient temperature.

An experimental glow curve and deconvoluted curves calculated by the GlowFit program given in Fig.1. Thermal quenching effects have not been taken into account [12]. The glow curve of the natural sand sample exhibits a wide asymmetric glow peak at about 330°C (Fig.1.5). The glow curves of the natural sand samples but different origins reported earlier, exhibits also similar peaks at different temperatures [5][13][14]. We have analyzed the TL parameters using the GlowFit program. Glow curve fitting analysis reveals that the glow curve is best fitted with three glow peaks (Fig.1, 1-3). FOM=2.06 %. Activation energy is one of the main trapping parameters that indicates the energy required to release thermally a trapped electron into the conduction band. According to the glow curve fitting result, activation energy values to each glow peak were as 0.96, 0.97 and 1.2 eV respectively. Calculated TL glow peaks located at 260°C, 318°C, 366°C. Corresponding frequency factors are within the physically meaningful ranges and with the values of 3.98×10^8 s^{-1}, 0.57×10^8 s^{-1}, and 1.06×10^9 s^{-1} respective to peak1, peak2 and peak3. As for the frequency factor, the frequency factor *s* (s^{-1}) should be of the order of magnitude of the Debye frequency, which has to do with the number of times per second that the trapped electron interacts with the phonons [15]. Many results reported by various authors over the years gave values of frequency factor in the range of 10^{10}-10^{13} s^{-1}. In some cases, anomalously high values of the frequency factor, accompanied by high values of the activation energy, were reported. G.C. Taylor and E. Lilley [16] reported a frequency factor of 2×10^{20} s^{-1} and activation energy of 2.06 eV of peak V of LiF:Mg,Ti (TLD-100). Fairchild et al. [17] suggested that the kinetics of this peak and other peaks with unusually large *s* might be complicated and the apparent first-order behavior is an approximation of a more complex kinetics situation. Chen and Hag-Yahya [18] presented a model of one trap and three recombination centers, one radiative and two non-radiative, to explain the possibility of high activation energy and very high frequency factor.

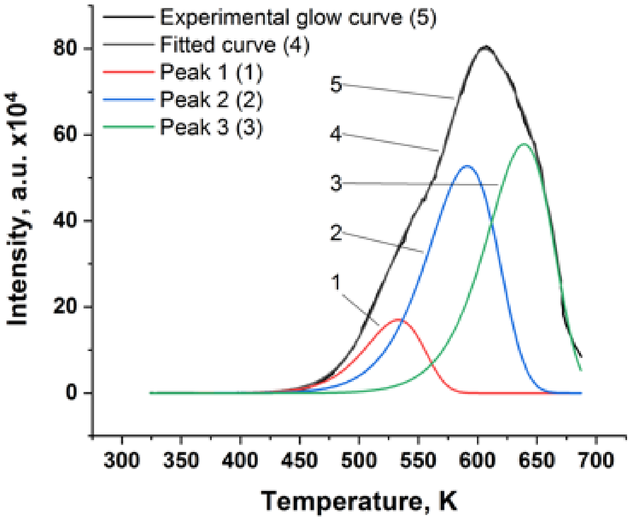

Fig. 1.Deconvolution of the TL glow curve of natural quartz using GlowFit into three components.

Mandowski [19] has offered another possible explanation of the occurrence of very high frequency factors and high activation energies in first-order-shaped TL peaks, which is based on the concept of cascade de-trapping.

In the literature, there are also reports on very small frequency factors (10^7 s^{-1}- 10^{10} s^{-1}), accompanied by small activation energies [5]. According to [15], typical values of frequency factor s (in s^{-1}) can be expected to range from 10^{11} to 10^{15} s^{-1}.

Preheating of quartz prior to irradiation has a drastic impact not only on the intensity of the TL signal but also on the structure of the entire glow curve [12]. Fig.2 describes the TL glow curves of quartz samples annealed at 600°C and then irradiated in the dose range of 2.24-22.4Gy. Though one could identify four different peaks due to severe overlapping of peaks at low and high temperature regions it would not be correct to assign them any parameters. GCA carried out by the GlowFit program five peaks for the best fit.

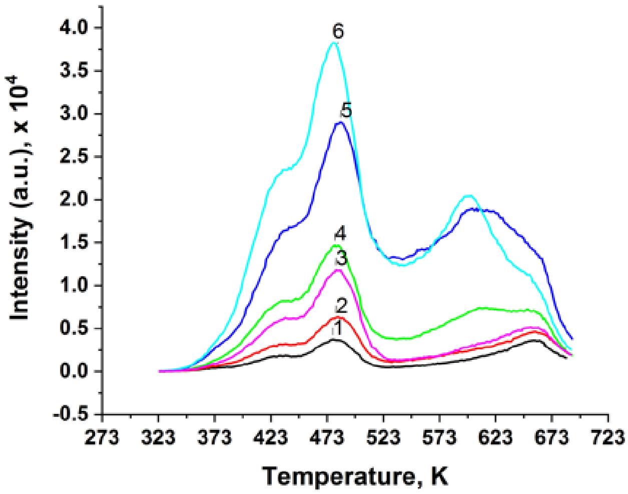

Fig. 2. Dose dependence of TL intensity irradiated quartz at different doses: (1) 2.24 Gy; (2)4.48 Gy; (3)7.72 Gy; (4)11.40 Gy: (5)17.92 Gy; (6)22.40 Gy. Natural quartz was heated at 650℃ for two hours prior to irradiation.

An experimental TL glow curve of quartz irradiated at 20 Gy and deconvoluted curves calculated by the GlowFit program given in Fig.3. TL parameters calculated by deconvolution for all glow curves shown in Fig.2 and average values are listed in Table 1. Over a wide range of irradiation doses, FOM values were below 2.0% for all glow curves. These FOM values are comparable to those seen in the glow curve analysis of quartz study by [5] in which FOM values of 1.35 %. Generally, for a good fit FOM value should be less than 3.5% [20].

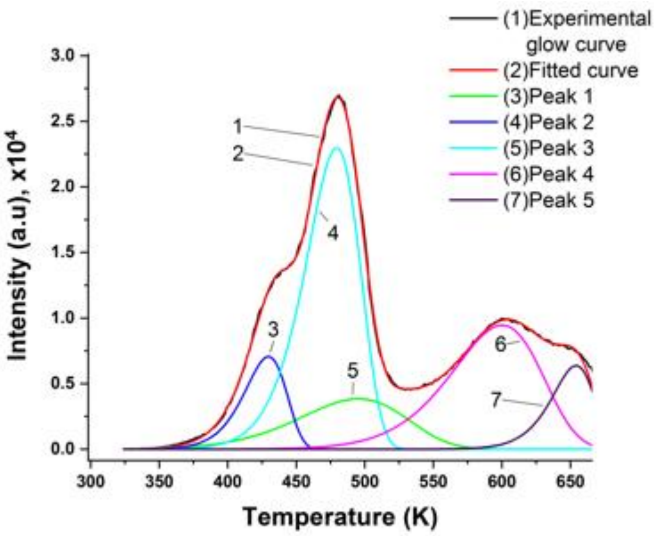

Fig. 3 Deconvolution of the TL glow curve of quartz irradiated at 20 Gy using GlowFit into five components. Natural quartz was heated at 650°C for two hours prior to irradiation.

Table 1. T_{max} parameters of deconvoluted TL glow curve components

Peak #	T_{max}, ^{0}C [current work]	T_{max}, ^{0}C [20]	T_{max}, ^{0}C [2]	T_{max}, ^{0}C [12]
Peak1	156±1	159	138	134
Peak2	207±2	202	214	200
Peak3	222±8	257	290	275
Peak4	333±10	303	337	295
Peak5	383±3	350	368	326

Table 1 illustrates T_{max} values of the peaks of natural quartz TL glow curves obtained by GCA including some of the literature dates. Though reported values are close to each other but still differ from each other because the origin of quartz as well as the heating rate used in those experiments was different. In addition to that, the referred values are obtained by deconvolution of thermally quenched glow curves. It means that if those values would have been reconstructed i.e. thermal quenching effect would have been taken into account, as it was described in [12], [21] those figures would be quite different especially in the high temperature zone.

3. Conclusions

The dosimetric characteristics and kinetic parameters of the sand sample were investigated using the TL technique. The TL glow curve of the natural, unheated quartz from a beach on the Caspian Sea coast of eastern Baku deconvoluted using the GlowFit program. It was found that, at least three peaks located at 260°C, 318°C, 366°C which corresponds to the electron traps with the depth of 0.96, 0.97 and 1.2 eV respectively. Calculated frequency factor values related to those centers are within the acceptable range and correlates with the figures reported earlier for the variety of sand samples. The discrepancies of those figures rather indicate for the individuality of sand samples from a different origin, pretreatment conditions, etc. Heating at 650℃ for two hours completely anneals those centers. The glow curves of preheated sand samples exhibit four poorly resolved peaks due to the overlapping of individual peaks at low and high temperature zones. The deconvolution of those glow curves enables to separate at least five peaks with the T_{max} close to the reported earlier in the literature.

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ПАРАМЕТРЫ ТЕРМОЛЮМИНЕСЦЕНЦИИ КВАРЦА, ИЗВЛЕЧЕННОГО ИЗ ПЛЯЖНОГО ПЕСКА

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Резюме: В данной работе дозиметрические характеристики и кинетические параметры образцов песка с пляжа в восточной части Баку на побережье Каспийского моря были исследованы с использованием метода TL. Кривая свечения TL натурального, необожженного кварца, разложено на составные части (деконволюция) с помощью программы GlowFit. Было обнаружено, что по меньшей мере три пика расположена при 260°C, 318°C, 366°C, что соответствуют электронным ловушкам с глубиной 0,96, 0,97 и 1,2 эВ соответственно. Рассчитанные значения частотного коэффициента, относящиеся к этим центрам, находятся в допустимых пределах и коррелируют с данными, представленными ранее для разнообразных образцов песка. Кривые свечения предварительно нагретых образцов песка показывают четыре плохо разрешенных пика из-за перекрытия отдельных пиков в зонах низких и высоких температур. Деконволюция этих кривых свечения позволяет разделить, по меньшей мере пять пиков с Tmax, близким к ранее опубликованному в литературе.

Ключевые слова: кварц; деконволюция; термолюминесценция

ÇİMƏRLİK QUMUNDAN ÇIXARILMIŞ KVARSIN TERMOLÜMİNSSENT PARAMETRLƏRİ

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Xülasə: Bu məqalədə, Bakının şərq hissəsindən, Xəzər dənizi sahilindəki çimərlikdən götürülmüş qum nümunələrinin tərkibindəki kvarsın dozimetrik xüsusiyyətləri və kinetik parametrləri TL üsulu ilə tədqiq edilmişdir. GlowFit proqramı istifadə edərək təbii, yandırılmamış kvarsın TL işıq spektri tərkib hissələrinə (deconvolusiya) ayrılmışdır. Aşkar edilmişdir ki, kvarsın mürəkkəb TL spektri, temperatur maksimumu 260°C, 318°C, 366°C nöqtələrində yerləşən ən azı üç spektrin cəmindən ibarətdir. Bu spektrlər dərinliyi müvafiq olaraq 0.96, 0.97 və 1.2 eV olan elektron tələlərinə yuğun gəlir. Bu mərkəzlərə uyğun olan tezlik faktorlarının hesablanmış qiymətləri qəbul edilən məhdudiyyətlər daxilində və qumun müxtəlif nümunələri üçün daha əvvəl təqdim olunmuş ədəbiyyat məlumatları ilə uyğunluq təşkil edir. Əvvəlcədən qızdırılan kvars nümunələrinin TL spektrində dörd müxtəlif pik müşahidə etmək mümükündür, lakin aşağı və yüksək temperatur zonalarında piklərin bir-birinə çox yaxın yerləşməsi səbəbindən onları dəqiq ayırmaq mümkün deyil. Dekonvulyasiya yolu ilə mürəkkəb spektri tərkib hissələrinə ayırdıqda isə onun beş, ayrı-ayrı spektrdən ibarət olduğunu görmək mümkündür. Bu nəticə əvvəllər ədəbiyyatda nəşr olunan məlumatlarla uyğunluq təşkil edir.

Açar sözlər: kvars; deconvolution; termolüminesensiya