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The Investigation of Kinetic Characterization of Sea Salt via Thermoluminescence Method

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Abstract

The calculation of the kinetic parameters of a thermoluminescence material (kinetic order (b), activation energy (E) and frequency factor (s)) by using the thermoluminescence (TL) method is extremely important in determining the kinetic characterization of the materials. Sodium Chloride (NaCl) is an inorganic salt. It is a crystal well known for its luminescent properties, with a simple cubic structure and its band gap is rather large (~ 8.5 eV). In this work, it was reported the TL response of the material in the range of 50– 400 ºC and calculated kinetic parameters of sea salt. Two glow peaks were observed at 100 ºC and 235 ºC in the TL glow curve of sea salt with a heating rate 2 ºC/s after X-ray irradiation. The T_m-T_{stop} method was used to determine the overlapping peaks under the main peak at 100 ºC. With the computerized glow curve deconvolution (CGCD) method, the peak analysis was performed. In addition, kinetic parameters were calculated using various heating rates and peak shape. The b = 1.5, E = 0.88 eV and s = $1.7x10^{11}$ s^{-1} values were calculated using the peak shape method.

Keywords — NaCl, Thermoluminescence, Kinetic Parameters, Heating rate, CGCD method

1. Introduction

In the crystals, the energy levels are found in the conduction and valence band energy levels, although they are prohibited according to the quantum theory. These energy levels are due to crystal structure defects or the presence of foreign atoms in the crystal. Electrons and holes resulting from the irradiation of the material with ionizing radiation can be trapped in the defect site, which is located in the forbidden energy range and is known as trap. When such a material is heated, these trapped electrons and holes may be retrapped or recombined with trapped holes or electrons, if they receive sufficient thermal energy. The plotted spectrum of the emitted light after radiative recombination and the corresponding temperature is called the glow curve. This spectrum is used to determine the TL kinetic parameters known as kinetic order (b), activation energy (E) and frequency factor (s). [1-5]. Sodium chloride, NaCl that is a good luminescent material is an inorganic salt that has a simple cubic structure and a very wide band gap (~ 8.5 eV). Besides applications in gastronomy, table salt might be of interest from a scientific point of view. Examination of the thermoluminescence properties of sodium chloride is possible only if it is sensitive to the presence of foreign substances in the structure. In literature, there are some studies on the luminescence properties of NaCl, [6-11]. However, to the best of our knowledge, no studies in literature have been found on the determination of the TL kinetics of sea salt.

In this study, the TL spectrum of sea salt exposed to X-ray was taken and kinetic parameters were calculated using different methods (peak shape and various heating rates).The T_m-T_{Stop} method was used to determine the location of the peaks under the main peak, and the E and s values were found by the CGCD method for the solved peak.

2. Material and Method

In this study, sea salt purchased from the local market was used, which can be used as an easy to use, low cost, reliable environmental dosimetry.

RA'94 TLD Reader-Analyzer system was used for obtaining TL spectra and Machlett OEG-50A X-ray tube (~ 30 Gy / min) was used for irradiation of samples. In order to prevent the loss of TL, experiments were carried out immediately after irradiation. In addition, a low heating rate (2 ºC /s) is preferred during experiments to minimize the temperature delay between the material and the material holder. The various heating rates and peak-shaped methods were used to calculate the TL kinetics of the main peak at 100 ºC for sea salt. In addition, T_m-T_{stop} method was applied to determine the peaks under the peak, and E and s values were calculated by the CGCD method for the analyzed peak. Information on the methods used is given below.

Various Heating Rates Method

In this method, while the linear heating rate (β) changes, the maximum intensity in the TL glow curve also changes the corresponding T_m maximum temperature. Increased heating rate causes T_m to shift towards higher temperature values.

The activation energy generated from the T_m corresponding to the two different heating rates is as follows:

$$E = k\frac{T_{M1}.T_{M2}}{T_{M1}-T_{M2}}\ln\left[\frac{\beta_1}{\beta_2}\left(\frac{T_{M2}}{T_{M1}}\right)^2\right] \quad (1)$$

Where T_{m1} and T_{m2} are the maximum peak temperatures corresponding to heating rates β_1 and β_2. s frequency factor can be calculated by replacing E in equation (2).

$$s = \frac{E}{k}\exp\left\{\left[T_{m2}ln\frac{T_{m2}^2}{\beta_2} - T_{m1}ln\frac{T_{m1}^2}{\beta_1}\right]/(T_{m1}-T_{m2})\right\} \quad (2)$$

An alternative way of computing the E and s values with this method is to draw a graph of $\ln\left(\frac{T_M^2}{\beta}\right)$ versus $1/kT_M$. While the activation energy E is calculated from the slope of the drawn graph, the s frequency factor can be found with equation (3) [12].

$$s = E\frac{e^{intercept}}{k} \quad (3)$$

T_{max}-T_{stop} Method

This method allows you to find the number and location of other peaks under a complex peak in the glow curve. The radiation-exposed material is heated at a linear heating rate to a temperature (T_{stop}) at the low temperature tail of the irradiation peak. The sample is cooled to room temperature and reheated to obtain the entirety of the remaining glow curve. The maximum peak temperature (T_{max}) in the radiation curve is recorded. T_{stop} temperature is increased by 5 ºC steps and the same process is repeated. In the graph plotted with the obtained T_{max} - T_{stop} values, the temperature of each flat region shows the presence and location of individual peaks under the main peak [2,13,14].

Peak Shape Method

In this method, the peak shape and geometric properties are used to calculate E, s and b kinetic parameters. The equations (4) given by Chen can be used in the calculation of the activation energy [15].

$$E_\alpha = c_\alpha\left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m) \quad (4)$$

Here α is replaced by δ, ω and τ. T_m is the maximum temperature of the peak, $\tau = T_m - T_1$ is the half-width of the peak on the low temperature side, $\delta = T_2 - T_m$ is the half-width of the peak on the high temperature side and $\omega = T_2 - T_1$ is the total half-width. c_α and b_α are defined as follows [2]:

$$c_\tau = 1.510 + 3.0(\mu - 0.42) \quad b_\tau = 1.58 + 4.2(\mu - 0.42)$$
$$c_\delta = 0.976 + 7.3(\mu - 0.42) \quad b_\delta = 0$$
$$c_\omega = 2.52 + 10.2(\mu - 0.42) \quad b_\omega = 1 \quad (5)$$

The μ=δ/ω is the geometric shape or symmetry factor. If μ=0.42, the first degree TL peak can be called. For second degree peaks, μ=0.52. In this method, the frequency factor s can be calculated by equation (6) [16].

$$s = \frac{\beta E}{kT_m^2}exp\left(\frac{E}{kT_m}\right)[1 + (b-1)\,\Delta_m]^{-1} \quad (6)$$

3. Result and Discussion

The thermoluminescence spectrum of the sample of sea salt exposed to X-rays was taken at a heating rate of 2 ºC/s. After irradiation for 15 min, in the spectrum of 50-400 ºC temperature range (Figure 1), two TL peaks were observed, one at 100 ºC and the other at 235 ºC.

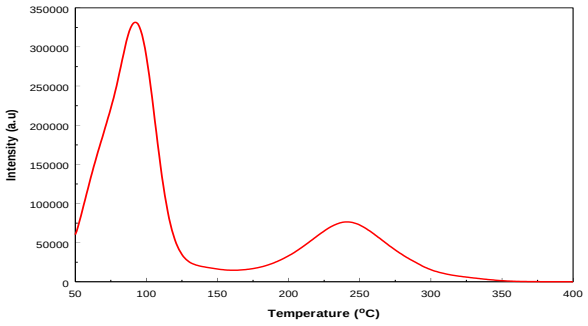


Figure 1 Glow curve of the salt sample after X-ray irradiation for 15 min with a heating rate of 2 ºC / s.

The increase in the irradiation time, and therefore the glow curves obtained by irradiation of the material at different doses are given in Figure 2. The slide of the curves along

with the increase of the dose indicates that the TL peak is not first degree. Moreover, the fact that the shape of the glow curve does not change depending on the dose increase shows that the curve is reproducible [17,18].

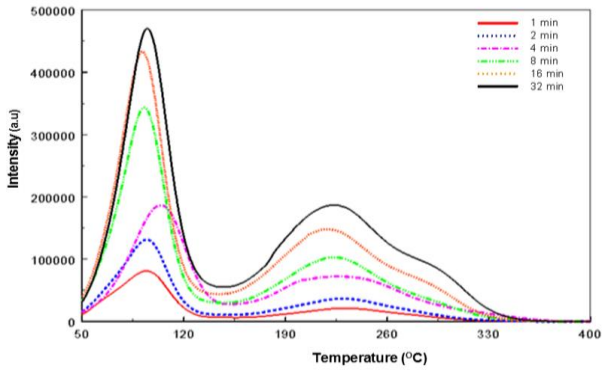


Figure 2 Glow curves obtained by changing the irradiation time under a constant heating rate of 2 °C/s.

When the material was irradiated for 1-32 min, peak intensity radiation increased with desire, but saturation did not reach. In order to generate the dose-response curve, which is an important feature for TLD dosimeters, the sample was exposed to a higher dose of X-rays and a curve of Figure 3 was formed with the received TL spectra for peak 1.

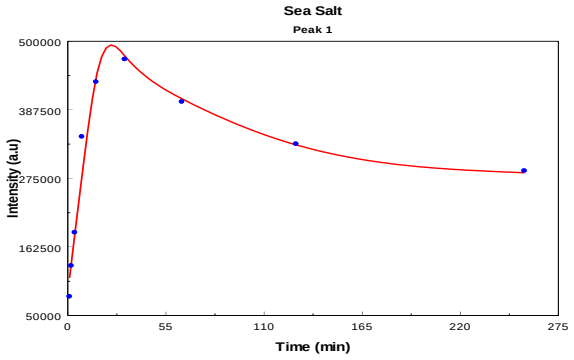


Figure 3 The dose-response curve for salt.

This obtained curve shows the dose dependence of the TL peak at 100 °C TL of the salt sample exposed to the X-ray at higher doses (2000-4000 Gy). As can be appreciated from the curves, the salt sample reached saturation for subsequent doses of approximately 3000 Gy, and a TL intensity that was proportional to the doses exposed was not achieved.

The dependence of the glow curve on the heating rate as well as the variation of the dose is also investigated. For this purpose, the heating rate was changed in the range of 1-5 °C / s, and the obtained glow curves are given in Figure 4.

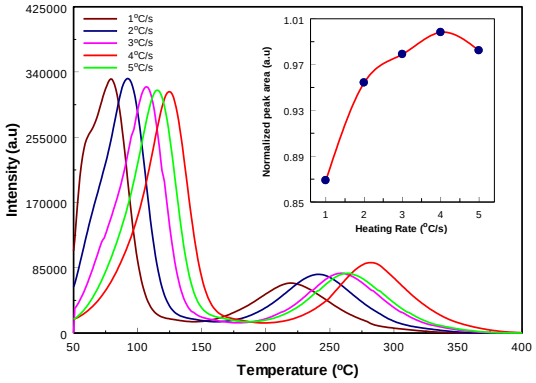


Figure 4 Change of TL spectrum depending on heating rate under constant irradiation duration of 5 min.

As the heating rate increases, the TL peaks at 100 °C and 235 °C are observed towards higher temperatures. This temperature shift is delayed in the heat exchange between the sample in the TLD system and the heating plate [2,15]. The heating rate was varied from 1-10 °C/s to determine E and s by various heating rates method. The plot of $\ln(T_m^2/\beta)$ depending $1/kT_m$ is directly calculated (Figure 5) with E value of 0.99 eV. T_m-T_{stop} method was applied to identify other peaks below at the 100 °C peak (Figure 6).

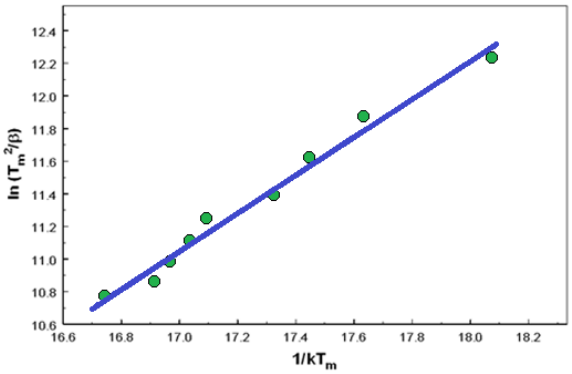
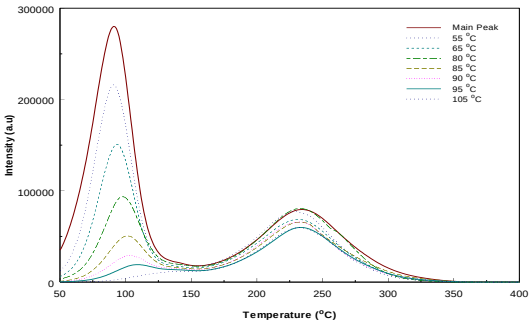


Figure 5 The change of $\ln(T_m^2/\beta)$ depending on $1/kT_m$



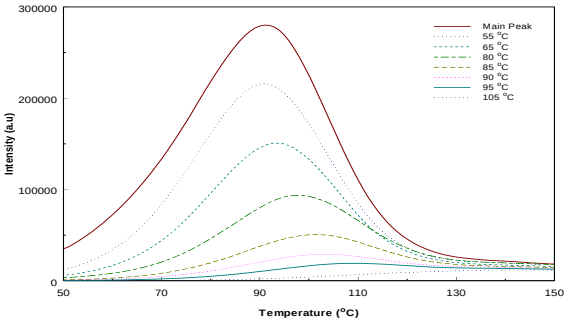


Figure 6 The glow curves of NaCI for different T_{stop} values.

It was determined that there are three different peaks under the main peak in the plot drawn between T_{max} corresponding to the T_{stop} values between 55-105 °C (Figure 7).

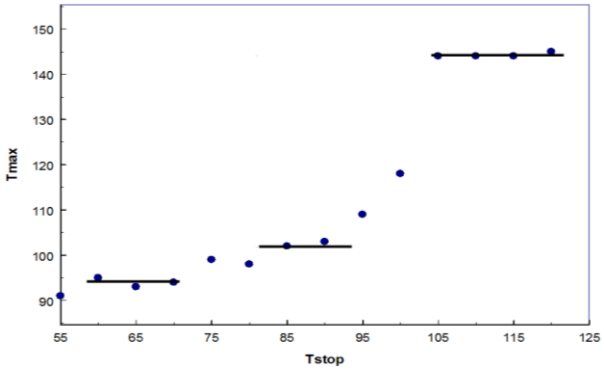


Figure 7 Locations of possible individual peaks reached by the T_{max}-T_{stop} method.

In addition to the various heating rates method, the kinetic parameters were calculated using the peak-shaped method. The obtained data are given in Table 1.

Table 1. Kinetic parameters calculated with peak shape and various heating rate methods.

METHOD	b	E (eV)	E_ω (eV)	E_δ (eV)	E_τ (eV)	s (s^{-1})
Peak Shape	1.5	0.884	0.893	0.877	0.882	$1.7x10^{11}$
Various Heating Rate	-	0.997	-	-	-	$1.5x10^{11}$

The Computerized Glow Curve analysis method (CGCD) was used to analyze TL glow curve of sea salt. Taking into consideration the T_m-T_{stop} data, it seen that there are three peaks under the 100 °C peak (Figure 8) [19]. The E and s values determined for each of these peaks are given in Table 2.

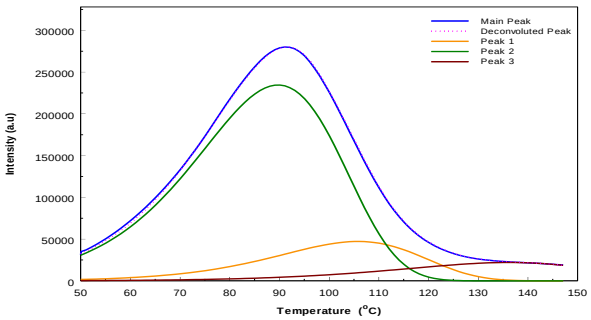


Figure 8 The analysis of experimental peak with CGCD method.

Table2. Peaks fitted by the CGCD method for the first peak and calculated kinetic parameters.

Peak Number	Max Temp. T_m (°C)	Aktivation Energy (eV)	Frequency Factor (s^{-1})
1	90	0.7412	$2.55x10^9$
2	106	0.8098	$7.56x10^9$
3	146	0.6891	$2.96x10^7$
FOM:%0.83			

4. Conclusion

In this study, the TL spectrum obtained from X-ray exposure of sea salt purchased from the domestic market was investigated. Activation energy, kinetic order and frequency factor (E, b and s) values of TL peak at 100 °C of sea salt were calculated by different methods. T_m-T_{stop} and CGCD methods are used in this main peak analysis at 100 °C. From the data obtained, it is seen that there are three different peaks under the main peak. In the CGCD method, the FOM value, which is a sign of agreement between experimental and theoretical data, is found to be 0.83%. E, s and b values of peak at 100 °C were calculated using peak shape and various heating rate methods. It seen that the value of E obtained from data is between 0.87-0.99 eV.

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