

DETERMINATION OF THE KINETIC PARAMETERS OF BeO THERMOLUMINESCENT SAMPLES USING DIFFERENT METHODS

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ABSTRACT

The objective of this work was to determine the kinetic parameters of BeO thermoluminescent (TL) samples. The knowledge of the kinetic parameters is important for the general description of the physical characteristics of a thermoluminescent material. Using a linear heating rate of 5K/s^{-1} , the BeO peak temperatures obtained were (474.7 ± 1.2) K and (620.5 ± 1.2) K, respectively, for the first and second TL peaks. The peak shape and the glow curve area measurement methods and the Urbach formula have been used for the trap parameter determination. A kinetic order of about two was determined for the first peak, whereas the second peak followed the first-order kinetics according to the geometrical factor. The energy activation values obtained using different kinds of measurements are in good agreement, including the Kitis method for deconvolution of the glow curve. Furthermore the results agree with those presented by other authors.

1. INTRODUCTION

The field of thermoluminescent dosimetry is widely used in personal dosimetry and year by year new materials are studied as possible thermoluminescent materials with the intention of having a material more equivalent to biological tissue, and therefore it is necessary to know all the physical characteristic of the material, as for example the kinetic parameters.

One of these materials is the Beryllium Oxide (BeO). It has an effective atomic number of approximately 7.22, what is similar to the effective atomic number of biological tissue ($Z_{\text{eff}} \sim 7,6$), has a linearity of response of six orders of magnitude ($5\mu\text{Gy}$ until 5Gy), has high sensitivity to mechanical stress, is insensitive to moisture (when in pellet), and low cost of production due to the wide use in the electronic and aerospace industries. However, BeO response presents high fading stimulated by white light, and should preferably be handled under red or yellow light (VIJ, SINGH, 1997; SOMMER *et al*, 2008; SOUZA *et al*, 2014).

This work reports on BeO in relation to its kinetic parameters which are important in the general description of the physical characteristics of a thermoluminescent material.

2. MATERIALS AND METHODS

The study was performed using ceramic BeO in disc form with (4.004 ± 0.003) mm of diameter, (0.771 ± 0.003) mm of thickness and (27.184 ± 0.015) mg of mass. An x-ray diffraction analysis showed that the main impurities are Al (350 ppm), K (749 ppm) and

Si (801 ppm) (GROPPO, 2013). The thermal treatment at 500°C for 15 min was used throughout the experiments, in order to erase any residual information before the subsequent irradiation. Figure 1 shows an example of BeO glow curve obtained with a linear heating rate of 5.0 K/s and a test dose of 464.8 mGy from an x-rays system of quality RQR 8 (100kV, 10mA; CSR of 3,97 mmAl and additional filtration of 3,2 mmAl).

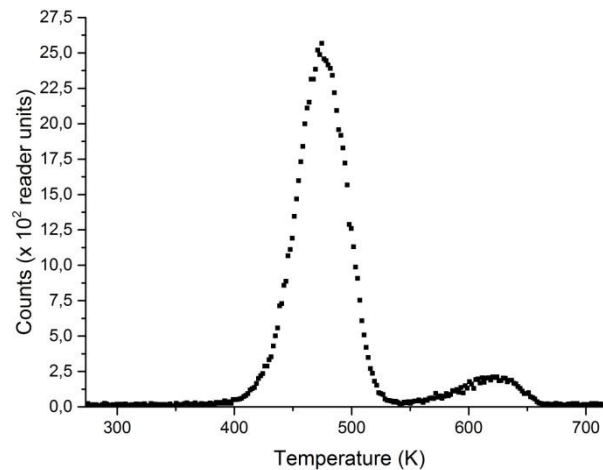


Figure 1: BeO glow curve obtained with a linear heating rate of 5.0 K/s and a test dose of 464.8 mGy of x-rays (RQR 8).

The experimental apparatus used to read out the TL emission and to record the glow curve is based on a system RISÖ TL/OSL-DA20. For thermal treatment an oven type muffin model MFLO1000 of Provecto Analítica was utilized.

3.1. Methods for determining the kinetic parameters

For determination of the frequency factor, the Chen's method was used and for the determination of the activation energy the following methods were used:

- Urbach's method;
- Peak shape methods:
 - Chen's method;
 - Grosswiener's method;
 - Lushchik's method;
 - Halperin and Braner's method;
 - Chen's additional formulae;
- The area measurement method.

3.1.1. Urbach's method

This method can be used with a first approximation for the evaluation of activation energy. Urbach empirically obtained an expression while studying KCl and he fixed the frequency factor as 10^9 s^{-1} . The equation of this method is:

$$E = TM/500 \quad (1)$$

where T_M is peak temperature (FURETTA, 2003; CHEN, PAGONIS, 2011).

3.1.2. Peak shape methods

The methods that fall under this terminology used a few points of the TL emission to determine the kinetic parameters. These points are the peak temperature (T_M) and the temperatures corresponding to the half of the peak intensity, with T_1 for temperature lower than T_M and T_2 for temperature higher than T_M (FURETTA, 2003; CHEN, PAGONIS, 2011). A scheme is illustrated in Figure 2.

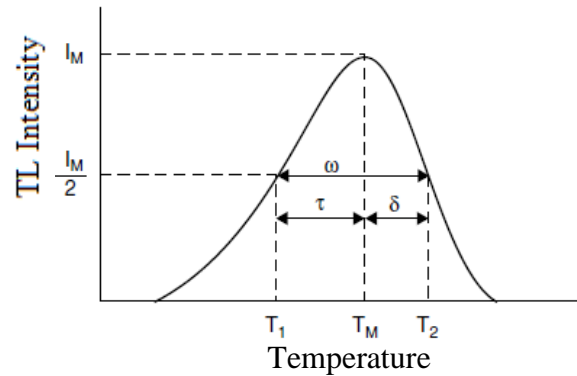


Figure 2: Parameters used in peak shape methods (CHEN, PAGONIS, 2011).

With the temperatures it is possible to obtain other parameters that facilitate the calculations:

$$\omega = T_2 - T_1 \quad \tau = T_M - T_1 \quad \delta = T_2 - T_M \quad \mu = \frac{\delta}{\omega} \quad (2)$$

3.1.2.1. Chen's method

This method considers that the kinetic order b of the TL peak can vary, this is, the equations that describe the behavior of TL emission are of general order, and the kinetics order is related to the geometric factor, Figure 3.

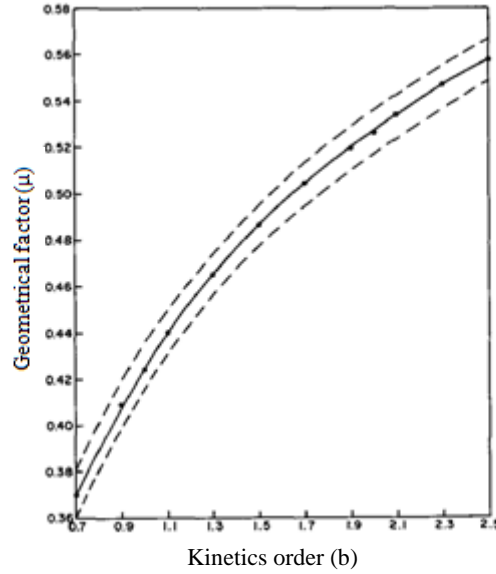


Figure 3: Geometrical factor versus kinetics order (CHEN, 1969).

With these assumptions and with the parameter of peak shape, the equations that determine the activation energy and the frequency factor are:

$$E_{\tau} = \left\{ [1.51 + 3 \times (\mu - 0.42)] \times \frac{kT_M^2}{\tau} \right\} - \{ [1.58 + 4.2 \times (\mu - 0.42)] \times 2kT_M \} \quad (3)$$

$$E_{\delta} = [0.976 + 7.3 \times (\mu - 0.42)] \times \frac{kT_M^2}{\delta} \quad (4)$$

$$E_{\omega} = \left\{ [2.55 + 10.2 \times (\mu - 0.42)] \times \frac{kT_M^2}{\omega} \right\} - 2kT_M \quad (5)$$

$$s = \frac{\beta E}{kT_M^2} \times \left[e^{\left(\frac{-E}{kT_M} \right)} \times \left(1 + (b - 1) \times \frac{2kT_M}{E} \right) \right]^{-1} \quad (6)$$

where E_{τ} , E_{δ} e E_{ω} are the activation energies in keV, using the parameter of peak shape, and s is the frequency factor in s^{-1} . The other parameters were defined previously (FURETTA, 2003; CHEN, PAGONIS, 2011).

3.1.2.2. Grosswiner's method

This method was deduced starting from an asymptotic series, to kinetics of first-order and second-order, and considering only the parameters T_M , T_1 e τ .

$$E_{\tau} = \frac{\alpha k T_1 T_M}{\tau} \quad (7)$$

where α has values of 1.41 and 1.68 for kinetics of first-order and second-order, respectively (FURETTA, 2003; CHEN, PAGONIS, 2011).

3.1.2.3. Lushchik's method

This method considers that the area under the TL peak on slope is equal to the area of a triangle that has the same height and width at half-height; that kinetic order is only of first or second-order and using the parameter δ . The equations for first-order and second-order kinetics (FURETTA, 2003; CHEN, PAGONIS, 2011) are respectively:

$$E_{\delta} = 0.976 \times \frac{kT_M^2}{\delta} \quad (8)$$

$$E_{\delta} = 1.706 \times \frac{kT_M^2}{\delta} \quad (9)$$

3.1.2.4. Halperian and Braner's method

This method uses values of T_M and T_1 to get the equations for first-order and second-order kinetics, respectively (FURETTA, 2003; CHEN, PAGONIS, 2011):

$$E_{\tau} = 1.52 \frac{kT_M^2}{\tau} - 3.16kT_M \quad (10)$$

$$E_{\tau} = 1.813 \frac{kT_M^2}{\tau} - 4kT_M \quad (11)$$

3.1.2.5. Chen's additional method

In this method, Chen used a width at half-height and only for first-order and second-order kinetics. To distinguish this method from that method Chen previous by also used, the parameter ω was denoted as ω' , but both have the same value (FURETTA, 2003; CHEN, PAGONIS, 2011).

$$E_{\omega'} = \frac{2.29kT_M}{\omega} \quad (12)$$

$$E_{\omega'} = 2kT_M \times \left(1.756 \times \frac{T_M}{\omega} - 1 \right) \quad (13)$$

3.1.3. The area measurement method

This method considers the area under the TL peak emission. When setting the limits of integration with T and T_f , where T is variable and T_f is fixed and corresponds to the end of the peak. The equations resulting for the cases of first-order and second-order kinetics are respectively:

$$\ln \left[\frac{I}{\int_{T_f}^T I dT} \right] = \ln \left(\frac{s}{\beta} \right) - \frac{E}{kT} \quad (13)$$

$$\ln \left[\frac{I}{\int_T^{T_f} I dT} \right] = \ln \left(\frac{s'}{\beta} \right) - \frac{E}{kT} \quad (14)$$

where $\ln \left[\frac{I}{\int_T^{T_f} I dT} \right]$ and $\ln \left[\frac{I}{\int_T^{T_f} I dT} \right]^n$ are linear functions of $\frac{1}{kT}$, with angular coefficient equal to $-E$; the point of interception of axis equal to $\ln \left(\frac{s'}{\beta} \right)$ for the case of first-order kinetics and $\ln \left(\frac{s'}{\beta} \right)$ for the case of second-order kinetics, β is the heating rate, $s' = \beta e^{\text{Intercept value}}$ and b is the kinetic order (FURETTA, 2003; CHEN, PAGONIS, 2011).

3.2. Deconvolution

The deconvolution is a mathematical method to create a curve using some theoretically and/or experimentally determined parameters. In this work the deconvolution process was used to verify if the kinetics parameters determined with various methods are consistent with each other by comparing with the experimentally curve of TL emission. The method used was developed by Kitis (CHEN, PAGONIS, 2011) and the equations are:

Case of first-order kinetics:

$$I(T) = I_m \exp \left[1 + \Delta - \frac{T^2}{T_M^2} \left(1 - \frac{2kT_M}{E} \right) \exp(\Delta) - \frac{2kT_M}{E} \right] \quad (15)$$

Case of second-order kinetics or general order kinetics:

$$I(T) = I_m b^{\left(\frac{b}{b-1}\right)} \exp(\Delta) \left\{ Z_M + (b-1) \left(1 - \frac{2kT}{E} \right) \left[\frac{T^2}{T_M^2} \exp(\Delta) \right] \right\}^{\left(\frac{-b}{b-1}\right)} \quad (16)$$

with

$$Z_M = 1 + \frac{(b-1)2kT_M}{E} \quad (17)$$

$$\Delta = \frac{E(T-T_M)}{kTT_M} \quad (18)$$

where I_m is the maximum peak TL intensity obtained experimentally, k is the constant of Boltzmann in $eV \cdot K^{-1}$, T is the temperature in K, T_M is the temperature at the maximum peak intensity in K, E is the activation energy in eV and b is the kinetic order of peak for all the equations (FURETTA, 2003; CHEN, PAGONIS, 2011).

4. RESULTS AND DISCUSSION

The results were obtained using the described methods. In Table 1 are the values obtained from the TL emission curve, of temperatures, where the maximum intensity of the TL

emission occurs and at half of the maximum intensity of the TL emission. In Table 2 are presented the parameters of the peak shape methods calculated with Equation (2).

Table 1: Maximum intensity temperature (T_M) and temperature at half of the maximum intensity (T_1 e T_2) of BeO TL peaks.

TL Peak	T_M (K)	T_1 (K)	T_2 (K)
First	474.7 ± 1.2	449.5 ± 1.2	500.0 ± 1.2
Second	620.5 ± 1.2	586.3 ± 1.2	645.8 ± 1.2

Table 2: Parameters used in peak shape methods.

TL Peak	ω (K) ($T_2 - T_1$)	δ (K) ($T_2 - T_M$)	τ (K) ($T_2 - T_1$)	μ (δ / ω)
First	50.40 ± 0.13	25.20 ± 0.13	25.20 ± 0.13	0.500 ± 0.003
Second	59.40 ± 0.13	25.20 ± 0.13	34.20 ± 0.13	0.424 ± 0.003

Using the area measurement method, under the TL curve for the fitting of the TL curves of BeO it was considered that the kinetic order of the first TL peak is between 1.0 and 2.0, and of the second TL peak between 0.7 and 2.0. The results of the fitting are shown in Figure 4.

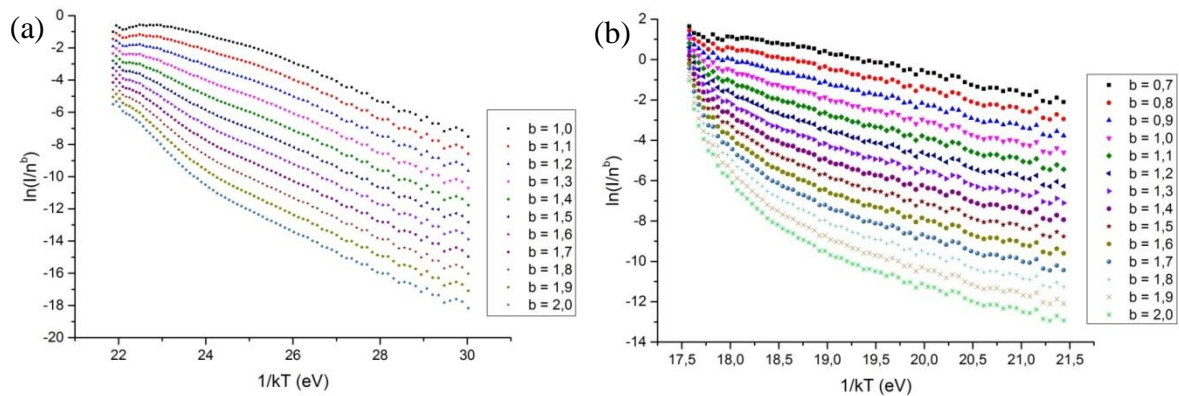


Figure 4: Determination of the kinetics order of (a) first TL peak and of (b) second TL peak of BeO using the area measurement method.

To determine the best linear fit, and consequently the kinetic order, the correlation factor was considered close to 1, as it may be observed in Figure 5.

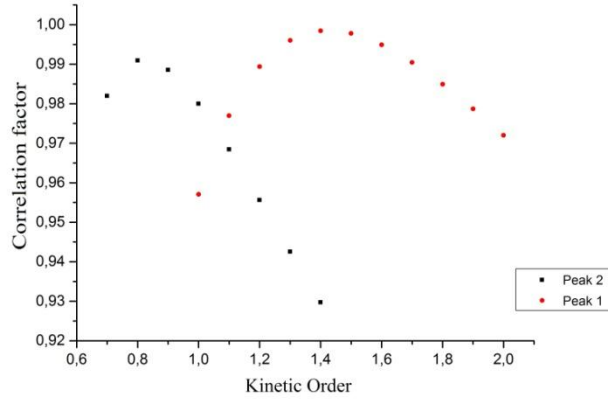


Figure 5: Correlation factor versus kinetic order of TL peaks 1 and 2 of BeO.

The value of the kinetic order for the first TL peak is (1.40 ± 0.20) , and for the second peak it is (0.80 ± 0.20) .

The values of the activation energy and of the frequency factor determined using the described methods are indicated in Tables 3 and 4; in Tables 5 and 6 are shown the values obtained by Bacci *et al* (1989).

Table 3: Activation energy and frequency factor for the first TL peak of BeO.

Method	First TL peak		
	Activation energy (eV)	Frequency factor (s^{-1})	Kinetic order
Urbach	0.9495 ± 0.0004	10^9	1
Grosswiener	1.226 ± 0.006	$(3.07 \pm 0.21) \times 10^{12}$	2
Lushchik	1.315 ± 0.007	$(2.89 \pm 0.04) \times 10^{13}$	2
Halperin e Braner	1.234 ± 0.007	$(3.72 \pm 0.06) \times 10^{12}$	2
Area	1.149 ± 0.005	$(4.53 \pm 0.04) \times 10^{11}$	1.40 ± 0.20
Chen (ω)	1.204 ± 0.012	$(1.74 \pm 0.03) \times 10^{12}$	1.60 ± 0.10
(τ)	1.19 ± 0.02	$(1.294 \pm 0.021) \times 10^{12}$	1.60 ± 0.10
(δ)	1.202 ± 0.017	$(1.682 \pm 0.021) \times 10^{12}$	1.60 ± 0.10
(ω')	1.2715 ± 0.0010	$(9.715 \pm 0.015) \times 10^{12}$	2

Table 4: Activation energy and frequency factor for the second TL peak of BeO

Method	Second TL peak		
	Activation energy (eV)	Frequency factor (s ⁻¹)	Kinetic order
Urbach	1.2411 ± 0.0004	10 ⁹	1
Grosswiener	1.293 ± 0.006	(6.14 ± 0.09) × 10 ⁹	1
Lushchik	1.285 ± 0.012	(5.31 ± 0.08) × 10 ⁹	1
Halperin e Braner	1.306 ± 0.007	(7.93 ± 0.10) × 10 ⁹	1
Area	1.240 ± 0.012	(2.13 ± 0.03) × 10 ⁹	0.80 ± 0.20
Chen (ω)	1.325 ± 0.014	(1.152 ± 0.021) × 10 ¹⁰	1.00 ± 0.10
(τ)	1.317 ± 0.014	(8.048 ± 0.010) × 10 ⁹	1.00 ± 0.10
(δ)	1.326 ± 0.004	(1.174 ± 0.022) × 10 ¹⁰	1.00 ± 0.10
(ω')	1.2793 ± 0.0011	(4.73 ± 0.07) × 10 ⁹	1

Table 5: Activation energy and frequency factor for the first TL peak of BeO obtained by Bacci et al (1989).

Method	First TL peak		
	Activation energy (eV)	Frequency factor (s ⁻¹)	Kinetic order
Urbach	0.99 ± 0,01	10 ⁹	
Grosswiener	1.47 ± 0,02	(1.0 ± 0.2) × 10 ¹⁵	2
Lushchik	1.55 ± 0,02	(7.1 ± 0.3) × 10 ¹⁵	2
Halperin e Braner	1.49 ± 0,03	(1.6 ± 0.2) × 10 ¹⁵	2
Area	1.14 ± 0,01	(2.4 ± 0.5) × 10 ¹⁴	1.61 ± 0.04
Chen (ω)	1.45 ± 0,05	(6.4 ± 0.2) × 10 ¹⁴	1.7 ± 0.2
(τ)	1.45 ± 0,05	(6.4 ± 0.1) × 10 ¹⁴	1.7 ± 0.2
(δ)	1.43 ± 0,05	(3.9 ± 0.3) × 10 ¹⁴	1.7 ± 0.2
(ω')	1.52 ± 0,01	(3.4 ± 0.2) × 10 ¹⁴	2

Table 6: Activation energy and frequency factor for the second TL peak of BeO obtained by Bacci *et al* (1989).

Method	Second TL peak		
	Activation energy (eV)	Frequency factor (s ⁻¹)	Kinetic order
Urbach	1.28 ± 0.01	10 ⁹	
Grosswiener	1.24 ± 0.05	(3.1 ± 0.4) × 10 ⁹	1
Lushchik	1.36 ± 0.06	(3.0 ± 0.2) × 10 ⁹	1
Halperin e Braner	1.25 ± 0.06	(3.7 ± 0.4) × 10 ⁹	1
Area	1.27 ± 0.03	(5.4 ± 0.2) × 10 ⁹	1.0 ± 0.2
Chen (ω)	1.19 ± 0.08	(1.2 ± 0.2) × 10 ⁹	1.0 ± 0.1
(τ)	1.19 ± 0.07	(1.2 ± 0.5) × 10 ⁹	1.0 ± 0.1
(δ)	1.16 ± 0.09	(0.7 ± 0.1) × 10 ⁹	1.0 ± 0.1
(ω')	1.29 ± 0.05	(7.9 ± 0.2) × 10 ⁹	1

Analyzing the results of Tables 3 and 4 it is possible to see the agreement of values obtained with different methods. The values obtained with the peak shape and area measurement methods are more in agreement with each other than the Urbach's method for the first TL peak. This occurs because Urbach considered the value of the frequency factor as 10⁹ s⁻¹ when developing his method (BACCI *et al*, 1989; CHEN, McKEEVER, 1997; FURETTA, 2003).

According to Chen, the values of activation energy involving δ and ω result in an inadequate evaluation, where the equations using τ are more correct (BACCI *et al*, 1989).

When comparing the values of Tables 3, 4, 5 and 6 it may be concluded that the activation energies and the frequency factors do not agree. This occurs because the BeO samples used in this work have impurities that do not exist in the samples studied by Bacci *et al* (1989) that influence the types of traps present in the material. In Table 7 are presented the impurities found in the BeO samples tested in this work and those by Bacci *et al* (1989), for comparison.

Table 7: Impurities in of BeO samples.

	Impurities
(GROPPO, 2013)	Si, K, Fe, Al e Co
(BACCI <i>et al</i> , 1989)	Mg e Si

The deconvolution of the TL emission curve was obtained using the Equations 15, 16, 17 and 18, and considering the values of activation energy and frequency factor obtained with all the methods used in this work. The results are indicated in Figures 6 and 7.

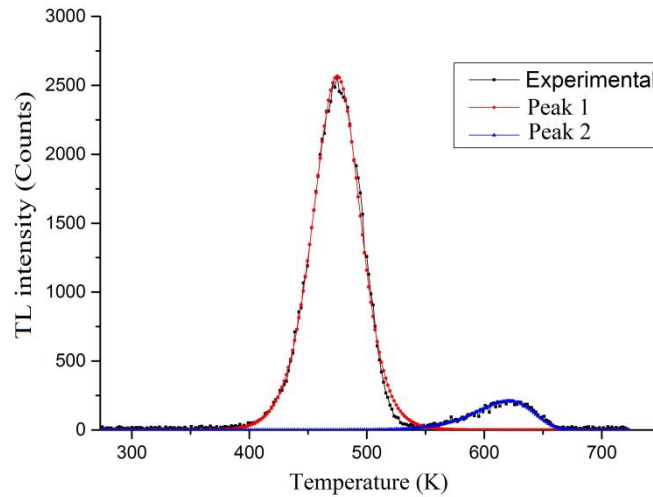


Figure 6: Deconvolution of the TL emission curve of BeO using the values of frequency factor and activation energy obtained by Chen's method and the parameter δ .

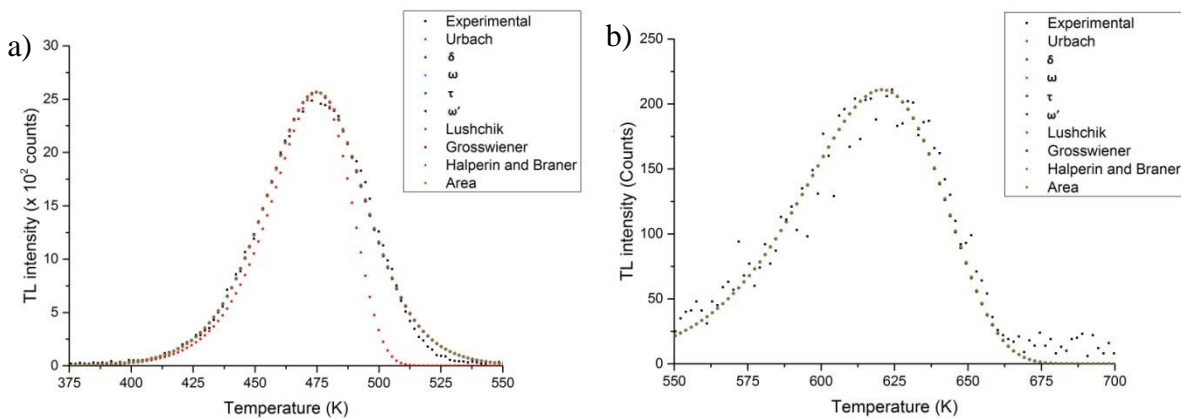


Figure 7: Deconvolution of (a) the first TL peak and (b) the second TL peak of TL emission curve of BeO, using the values of frequency factor and activation energy of Tables 3 and 4.

Comparing the curves obtained with the deconvolution, using the values of activation energy and frequency factor of Tables 3 and 4, it can be seen that there are no differences between them, except in the curve that used the kinetics parameters obtained with Urbach's method. Therefore, any determination method of the frequency factor and activation energy, except that of the Urbach's method, is acceptable.

5. CONCLUSIONS

The kinetics parameters of BeO correspond to the values obtained in all the methods, except by Urbach's method, what is evident in the deconvolution of the TL emission curve when compared with the TL emission curve obtained experimentally. The values of kinetics

parameters obtained in this work disagree with other studies, possibly because of the different impurities in the samples used in both studies.

The impurities interfere in the trap depth of the samples, so the impurities need to be considered in all samples to determine correctly the kinetics parameters.

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