Determination of electron trapping parameters: A revisit to Urbach’s formula

Thoudam Basanta Singh¹, Lisham Paris Chanu², R K Gartia²

¹Don Bosco College, Maram, Manipur, India-795015
²Department of Physics, Manipur University, Canchipur, Manipur, India-795003

*Email: thdambasanta@gmail.com

Abstract. Determination of electron trapping parameters in insulating as well as semi-insulating (SI) solids has remained an interesting rewarding field of research in solid state physics. The earliest formula for determination of the trap-depth \(E\) - the key parameter - was given by Urbach in 1948. Despite being one of the simples formula that has its own limitations, it is used even today. In this work we revisit the relevance of the formula at a time when whole curve fitting method has been the accepted method not only for evaluation of trap depth \(E\) but also other trap parameters like the frequency factor \(s\) and the order of kinetics \(b\). On the finer aspect of the work we test the historical formula for ZnO based phosphors and provide some insight into thermally stimulated processes (TSPs) as a whole. Finally, we present the philosophical implications of the historical formula by comparing the electron trap parameter \(E\) obtained by both the methods (Urbach and whole curve fitting).

1. Introduction

Urbach’s formula for determination of electron trapping parameter in solids is the first of its kind. It was proposed as early as 1948 for thermoluminescence (TL) [1]. It is one of the simplest formulas in solid state physics given as

\[
E = 23kT_m
\]

Or,

\[
E = \frac{T_m \text{(K)}}{500} 
\]

where \(E\) (in eV) is the trap depth; \(T_m\) is the peak temperature in absolute scale and \(k\) is the Boltzmann’s constant.

The formula was used in the beginning by many early workers of TL [2-3] and thermally stimulated current (TSC) [4-7].

Subsequent to the Urbach’s method, numerous methods were proposed by the workers devoted to theoretical approach to study the complex phenomenon that involves as many as eight parameters. The most important among them are the trap depth \(E\), the frequency factor \(s\) and the order of kinetics \(b\). It is to be noted that \(E\) and \(s\) are intrinsic parameters, while \(b\) is just an empirical one. However, at the present state of development for most practical purposes the description the phenomenon of TL by the three parameters \((E, s\) and \(b))\ has been accepted. The basic phenomenological equation that describes TL in this model referred as general order kinetics is given by Chen [8] as
\[ I(T) = n_0^b s' \exp \left( \frac{-E}{kT} \right) \left[ 1 + \frac{s' \tau_{m}^{b-1} (b-1)}{\beta} \int_{T_0}^{T} \exp \left( \frac{-E}{kT'} \right) \frac{1}{T'} \, dT' \right]^{\frac{-b}{b-1}} \quad \text{(2)} \]

where \( E \) is the trap-depth (eV), \( k \) is the Boltzmann’s constant (eV K\(^{-1}\)), \( T \) is the absolute temperature (K), \( T = T_0 + \beta t \), where \( \beta = \frac{dT}{dt} \) is the heating rate, \( t \) is the time (s), \( T_0 \) is the temperature at time \( t = 0 \) (in K), \( n_o \) is the number of trapped electrons at time \( t = 0 \) (in m\(^{-3}\)), \( b \) is the kinetic order (a parameter with values typically between 1 and 2), \( s' \) is the so-called effective pre-exponential factor for general order kinetics with dimension (m\(^{3(b-1)}\)s\(^{-1}\)) and \( s'' = s' n_0^{b-1} \), an empirical parameter acting as an “effective frequency factor” for general-order kinetics (in s\(^{-1}\)).

It is to be noted that equation (2) is not valid for \( b = 1 \) and hence for \( b = 1 \) we compute the TL with \( b = 1.001 \). As of today, using equation (2) whole curve fitting under the name computerized glow curve deconvolution (CGCD) is the standard practice. The technique is well standardized by the community of TL dosimetry [9-11].

In a recent paper Chandrasekhar et al [12] have presented a critical account of Urbach’s formula by comparing the value of \( E \) with that obtained from rigorous CGCD. In this work we go a bit deep to explore the concept presented there by extending it to a rather wide range of temperature of thermal scan i.e. 77K to 700K for the case of ZnO based phosphors. Incidentally, ZnO being one of the earliest SI solid is the most extensively studied candidate for its technical potentialities [13-14]. The ultimate aim is to provide a philosophical implication of the fact of a direct correlation of two key parameters (\( E \) and \( T_m \)) of a group of thermally stimulated processes like TL, TSC and deep-level transient spectroscopy (DLTS). \( E \) is the most important intrinsic trapping parameter in all insulating and semi-insulating (SI) solids whereas \( T_m \) (K) is an easily observable experimental parameter. Further it must be kept in mind that \( T_m \) (K) is not constant but varies with the rate of heating (\( \beta \)) that is used in a broad range without much restriction (0.03 \( \leq \beta \leq 5 \) s\(^{-1}\)).

2. Experimental and theoretical technique

For low temperature TL data acquisition 25 mg of the material ZnO:Ga, (Phosphor Technology, Hertfordshire, England) is sprinkled on an aluminium test cavity of 20mm diameter and 2mm depth and cooled to 77 K. The sample is irradiated at LNT (-196°C / 77K) by e-beam (2.2 MeV) with a dose of 5kGy. Then it is placed in the thermoluminescence equipment, and, its glow curves are recorded with heating rate (\( \beta \)) = 0.05°s\(^{-1}\) between 77K and 225 K. The details have been described earlier [15-16].

Specifications of TL peaks used with reference used in as global data are given in table 1.

| Sl. No. | Material       | Heating rate (°C s\(^{-1}\)) | Reference |
|--------|----------------|-------------------------------|-----------|
| 1      | ZnO            | 5                             | [17]      |
| 2      | ZnO            | 2                             | [18]      |
| 3      | ZnO, ZnO:Co    | 5                             | [19]      |
| 4      | ZnO:Mg         | 5                             | [20]      |
| 5      | ZnO:Cr         | 6                             | [21]      |
| 6      | ZnO            | 6.7                           | [22]      |
| 7      | ZnO            | 4                             | [23]      |
| 8      | ZnO, ZnO:Yb    | 5                             | [24]      |
| 9      | ZnO, ZnO:Yb    | 5                             | [25]      |

Specifications of TL peaks with reference used in as global data are given in table 1.
The details for analysing high temperature TL data are given in the paper [26]. The details of the theoretical techniques used for deconvolution are given in the earlier paper of Gartia [27]. In CGCD the criteria of goodness-of-fit is generally the low value of figure of merit (FOM) [28-29], defined as

\[ FOM = \sum_{j=\text{start}}^{j=\text{stop}} \frac{100|y_j - y(x_j)|}{A} \]  

where \( j_{\text{start}} \) is the initial temperature in the fit region, \( j_{\text{stop}} \) the final temperature in the fit region, \( y_j \) the experimental TL intensity at temperature \( j \), \( y(x_j) \) the value of the fit found at temperature \( j \), \( A \) is the integral of the fitted glow curve. A low value of FOM is generally indicates the fit is good.

### 3. Results and discussion

The result of CGCD of TL curve of ZnO: Ga is shown in figure 1 and the best-fit parameters in table 2. The fitting is good as revealed by the value of the FOM. The plot of \( E \sim kT_m \) of the best-fit parameter is shown in figure 2. It gives the magnitude of the Urbach’s coefficient of equation (1) to be \((28.00 \pm 1.80)\).
In order to check this value, we have compiled the global data on trap depth ($E$) and the corresponding TL peak temperatures ($T_m$) of number of workers over the long period 1960 to 2017. The Urbach’s plot of the results is shown in figure 3. Barring one [22] in the rest of the cases the values of the coefficients are within the expected range giving an average value of $23.00 \pm 2.80$. Thus, the analysis of figure 3 where the Urbach’s coefficient is found to be 9.98 seems questionable [22].

![Figure 2. Urbach’s plot of ZnO based phosphor](image-url)
In other words, the value of Urbach’s coefficient can be used as a simple, rapid but powerful method of checking the physical basis of the analysis.

4. Philosophical implications of Urbach’s rule

Urbach’s rule philosophically can be summed up as

\[ E = X k T_m \]  

where \( X \) is the Urbach’s coefficient, \( k \) the Boltzmann’s constant and \( T_m \) the peak temperature in absolute scale. Unlike the original formula in a board sense \( X \) is not a universal constant. It depends upon the lattice property; being affected by activator and co-activators only marginally. Equation (4) in principle philosophically can be extended to all thermally stimulated processes like TSC and DLTS. It has been shown to be true for TSC [12].

As a check to our logical extension of Urbach’s formula to DLTS, that has been very widely acknowledged as a technique to characterize semiconductor we present the Urbach’s plot of the data of

![Urbach’s plot of ZnO based phosphor (Global data)](image-url)
GaN documented by Ngoepe et al. [30] (figure 4). The magnitude of Urbach’s coefficient in these cases comes out to be 18.00.

\[ y = 18.58x - 0.009 \]
\[ R^2 = 0.909 \]

**Figure 4. Urbach’s plot of GaN [30]**

5. Conclusion

TL is a complex phenomenon that requires as many as eight parameters to describe it. In spite of the complexity Urbach's formula does provide an easy estimate of the most important intrinsic trap parameter, the trap-depth \( (E) \) by just one parameter i.e. the peak temperature \( (T_m) \). The relation \( E = XkT_m \) may be considered universal for TL, TSL and DLTS as well, where \( 15 \leq X \leq 40 \) for the temperature range 77 to 700K.

**Acknowledgement**

R.K. Gartia is thankful to UGC, New Delhi for award of an Emeritus Fellowship in which L. Paris Chanu worked as an assistant. The authors are thankful to Phosphor Technology Ltd., Hertfordshire, England for providing the ZnO: Ga phosphor. Further we are thankful to Late Prof. Louis Rey, Aerial, France for allowing the use of his low temperature TL reader.

**References**

[1] Urbach F 1948 *Cornell Symposium* (Wiley, New-York) p115
[2] Halperin A and Branner A A1960 *Phys. Rev.* 117 408
[3] Bube R H, Dussel G A, Ho C T and Miller L D 1966 *J. Appl. Phys.* 37 21
[4] Miller L D and Bube R H 1970 *J. Appl. Phys.* 41 3687
[5] Dussel G A and Bube R H 1967 *Phys. Rev.* 155 764
[6] Castagne M, Bonnafe J, Manifacier J C and Fillard J P 1980 *J. Appl. Phys.* 51 4894
[7] Bonnafe J, Castagne M, Romestan J and Fillard J P 1981 *J. Phys. C: Solid State Phys.* 14 2465
[8] Chen R 1969 *J. Electrochem. Soc.* 116 1254
[9] Horowitz Y S and Yossain D 1995 *Radiat. Prot. Dosim.* 60 3
[10] Horowitz Y S and Moscovitch M 2013 *Radiat. Prot. Dosim.* 153 1
[11] Horowitz Y, Oster L and Eliyahu I 2018 *Radiat. Prot. Dosim.* 179 184
[12] Chandrasekhar N, Bishal K S and Gartia R K 2017 *J. Rare Earths* 35 733
[13] Look D C 2001 *Mater. Sci. Engin. B* 80 383
[14] Özgü Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S -J and Morkoç H 2005 *J. Appl. Phys.* 98 041301
[15] Rey L 2003 *Physica A* 323 67
[16] Rey L 2005 Radiat. Phys. Chem. 72 587
[17] Borbón-Nuñez H A, Iriqui-Razzón J L, Cruz-Vázquez C, Bernal R, Furetta C, Chernov V and Castano V M 2017 J. Mater. Sci. 52 5208
[18] Kalita J M and Wary G 2017 J. Elec. Materi. 46 4287
[19] Pushpa N and Kokila M K 2017 J. Lumin. 190 100
[20] Pushpa N, Kokila M K and Nagabhushana K R 2016 Nucl. Instrum. Methods Phys. Res. B 379 62
[21] Pushpa N, Kokila M K, Nagabhushana B M, Nagabhushana H and Jagannatha R A 2015 Bull. Mater. Sci. 38 1359
[22] Jagannatha R A, Kokila M K, Nagabhushana H, Rao J L, Shivakumara C, Nagabhushana B M and Chakradhar R P S 2011 Spectrochim. Acta Part A 81 59
[23] Manam J, Das S and Isaac A 2009 Ind. J. Phys. 83 1407
[24] Pal U, Meléndrez R, Chernov V and Barboza-Flores M 2008 J. Nanosci. Nanotech. 8 6513
[25] Pal U, Meléndrez R, Chernov V and Barboza-Flores M 2006 Appl. Phys. Lett. 89 183118
[26] Panda N R, Acharya B S, Basanta S Th and Gartia R K 2013 J. Lumin. 136 369
[27] Gartia R K 2009 Nucl. Instrum. Methods Phys. Res. B 267 2903
[28] Balian H G and Eddy N W 1997 Nucl. Instrum. Methods 145 389
[29] Misra S K and Eddy N W 1979 Nucl. Instrum. Methods 166 537
[30] Ngoepe P N N, Meyer W E, Auret F D, Omotoso E and Diale E M 2017 Mater. Sci. Semicond. Proces. 64 29