

**DEVELOPMENT OF UNDOPED, DOPED AND  
CODOPED BORON SILICATE COMPOSITE AS  
THERMOLUMINESCENT DOSIMETERS FOR  
MEDIUM AND HIGH DOSE LEVELS**

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THERMOLUMINESCENT DOSIMETERS FOR  
MEDIUM AND HIGH DOSE LEVELS**

by

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**Thesis submitted in fulfillment of the requirements  
for the degree of  
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**SPECIAL DEDICATION To:**

**My late Parents**

**My Siblings**

**Nisrin, Omer, Amina, Marjan, Fauzia, Ali**

**My Nephews and Nieces**

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## TABLE OF CONTENTS

ACKNOWLEDGMENT .....	ii
TABLE OF CONTENTS .....	ii
LIST OF TABLES .....	viii
LIST OF FIGURES .....	x
LIST OF ABBREVIATIONS .....	xv
LIST OF SYMBOLS .....	xvi
ABSTRAK .....	xviii
ABSTRACT .....	xx
<b>CHAPTER1: INTRODUCTION</b> .....	<b>1</b>
1.1 Introduction .....	1
1.2 Statement of the Problem .....	3
1.3 Objectives of the research .....	4
1.4 Scope of the research.....	4
1.5 Outline of thesis .....	5
<b>CHAPTER 2: LITERATURE REVIEW</b> .....	<b>6</b>
2.1 Introduction .....	6
2.2 Luminescence.....	6
2.2.1 Fluorescence .....	6
2.2.2 Phosphorescence.....	7

2.2.3	Model of thermoluminescence .....	8
2.3	Glow curve theory .....	10
2.3.1	First order kinetics .....	10
2.3.2	Second –order kinetics .....	12
2.3.3	General–Order Kinetic .....	13
2.4	Applications of the thermoluminescence .....	13
2.5	TLD characteristic and measurement .....	14
2.5.1	Annealing procedure .....	15
2.5.2	Glow curve .....	16
2.5.3	Glow curve analysis .....	16
2.5.4	Sensitivity .....	20
2.5.5	Dose response (linearity) .....	20
2.5.6	Reproducibility (reuse) and stability .....	22
2.5.7	Energy response.....	23
2.5.8	Fading .....	25
2.5.9	Minimum detectable dose.....	26
2.6	Effective atomic number $Z_{\text{eff}}$ .....	27
2.7	Previous work.....	28
<b>CHAPTER 3: METHODOLOGY AND INSTRUMENTS.....</b>		<b>34</b>
3.1	Introduction .....	34
3.2	Raw Chemical Materials .....	34
3.2.1	Zinc Oxide (ZnO).....	35
3.2.2	Boron trioxide or diboron trioxide ( $B_2O_3$ ).....	35
3.2.3	Silicon dioxide or Silica Oxide ( $SiO_2$ ).....	36

3.2.4	Copper oxide (Cu <sub>2</sub> O).....	37
3.2.5	Tin oxide or stannic oxide (SnO <sub>2</sub> ).....	38
3.3	Glass system preparation.....	38
3.3.1	Preparation SiO <sub>2</sub> using Rice Husk (RH) in the Laboratory.....	39
3.3.2	Preparation three types of glass samples .....	41
3.4	XRD analysis (X-ray diffraction).....	44
3.5	Field emission scanning electron Microscope (FESEM) analysis .....	45
3.6	Differential thermal analysis (DTA) .....	46
3.7	Annealing procedure .....	48
3.8	Samples exposure.....	49
3.8.1	Cobalt-60 gamma cell.....	49
3.8.2	Linear accelerator (LINAC) .....	49
3.9	TLD reader .....	51
3.10	Other Tools.....	53
3.10.1	Vacuum tweezers.....	53
3.10.2	Milling tool.....	54
3.10.3	Sensitive Electric Balance .....	54
<b>CHAPTER 4: RESULTS AND DISCUSSION .....</b>		<b>56</b>
4.1	Introduction .....	56
4.2	Glass Samples and Composition .....	56
4.3	X-ray Diffraction analysis (XRD).....	59
4.4	Differential thermal analysis (DTA) .....	60
4.5	Field emission scanning electron microscopy (FESEM) analysis .....	62
4.6	Effective atomic number (Z <sub>eff</sub> ) .....	67
4.7	Optimization of sample compositions.....	68

4.7.1	Undoped TL response zinc borate silica ZBS glasses phosphor.....	69
4.7.2	Optimization of Cu doped and Sn codoped ZBS .....	71
4.8	Annealing Procedure .....	74
4.8.1	Annealing Procedure for undoped composition .....	75
4.8.2	Annealing Procedure for Cu doped composition .....	75
4.8.3	Annealing Procedure for SnO <sub>2</sub> codoped composition.....	77
4.9	Temperature time profile (TTP) setting .....	79
4.9.1	Heating rate of undoped (ZBS) glass samples .....	80
4.9.2	Heating rate of doped (ZBS:Cu) glass samples.....	81
4.10	Dose-TL Response Relationship .....	84
4.10.1	Gamma ray cobalt- 60 irradiation.....	84
4.10.2	Electron and x-ray photon (LINAC) irradiation.....	85
4.10.3	Comparison between the optimum (codoped) sample and TLD 100.....	87
4.11	TL Sensitivity .....	89
4.12	Reproducibility .....	91
4.13	Minimum Detectable Dose (MDD).....	93
4.14	Thermal Fading Measurement .....	94
4.15	Measurement Optical Bleaching .....	96
4.16	Determination of kinetic Parameters using peaks shape method.....	98
4.17	Theoretical calculation of Photon Energy response .....	102
4.17.1	Theoretical calculation of photon energy response for ZBS .....	103
4.17.2	Theoretical calculation of photon energy response for ZBS:Cu .....	105
4.17.3	Theoretical calculation of photon energy response for ZBS:Cu.Sn .....	107
4.18	Outline of the findings.....	110



<b>CHAPTER 5: CONCLUSION</b> .....	111
5.1 Conclusion.....	111
5.2 Recommendations and Future Research .....	115
<b>REFERENCES</b> .....	116
<b>APPENDICES</b> .....	124

## LIST OF TABLES

	<b>Page</b>	
Table 2.1:	Values for the constants $C_{\alpha}$ and $b_{\alpha}$	18
Table 2.2:	Listed the characteristics of some key TL materials (dosimeters)	29
Table 4.1:	The raw materials and chemical compositions of prepared undoped glasses.	58
Table 4.2:	The raw materials and chemical compositions of prepared doped glasses	58
Table 4.3:	The raw materials and chemical compositions of prepared co doped glasses.	59
Table 4.4:	Results of DTA studies of present glasses samples.	61
Table 4.5:	Weight percentage of elements in ZBS.	66
Table 4.6:	Weight percentage of elements in ZBS:Cu.	66
Table 4.7:	Weight percentage of elements in ZBS:Cu.Sn.	67
Table 4.8:	Effective atomic number of the glass compositions for present work and previous works	68
Table 4.9:	Annealing temperature and time of present study compared with others.	79
Table 4.10:	Heating Rates of the compositions under study compared with other work.	83
Table 4.11:	The sensitivity of different TL materials for various types of energies.	90

Table 4.12:	The minimum detectable dose of different TL materials for various types of energies.	93
Table 4.13:	Fading characteristics exposed to sun light.	96
Table 4.14:	Fading characteristics exposed to fluorescent light.	98
Table 4.15:	Kinetic parameters of undoped, doped and codoped glass under study.	99
Table 4.16:	Activation energy and frequency factor of presented glass samples calculated by using Chen's equations.	100
Table 4.17:	Values of E and S for the compositions under study and some other works.	101
Table 4.18:	Mass energy absorption coefficient of ZBS at various energies.	103
Table 4.19:	Photon energy response and relative energy response of ZBS normalized at 1.25 MeV	104
Table 4.20:	Mass energy absorption coefficient of ZBS:Cu at various energies.	105
Table 4.21:	Photon energy response and relative energy response of ZBS:Cu normalized at 1.25 MeV.	106
Table 4.22:	Mass energy absorption coefficient of ZBS:Cu.Sn at various energies.	108
Table 4.23:	Photon energy response and relative energy response of ZBS:Cu.Sn normalized at 1.25 MeV.	109
Table 4.24:	Summarized of finding concerning for the examined compositions in this research.	110

## LIST OF FIGURES

	<b>Page</b>
Figure 2.1: Electron transitions involve in the processes of (a) fluorescence (b) phosphorescence.	7
Figure 2.2: A simple energy band model for thermoluminescence.	8
Figure 2.3: General TL glow curve, showing also the parameters discussed in the peak shape glow curve analysis methods.	19
Figure 2.4: Linearity curve of TL dosimeter.	21
Figure 2.5: Variation of relative photo energy response with energy.	25
Figure 3.1: Raw Chemical materials used for making glass samples.	39
Figure 3.2: Preparation SiO <sub>2</sub> by using raw material rice husk.	40
Figure 3.3: Furnaces used for melting and annealing samples in this study.	42
Figure 3.4: Flowchart of preparation and analysis glass samples in this research	43
Figure 3.5: Glass samples with (a) different concentration of doped Cu <sub>2</sub> O inside the annealing furnace, (b) the bulk of glass sample, (c) crush doped Cu <sub>2</sub> O sample, (d) TLDs glass samples inside the capsule ready to exposure.	44
Figure 3.6: XRD machine used to study the amorphous phase of glasses samples.	45
Figure 3.7: Photograph of the FE-SEM machine (JSM-6340F Model) used in this study.	46
Figure 3.8: Schematic principle of DTA system.	47
Figure 3.9: Computerized system of electric annealing oven.	48

Figure 3.10:	220 Excel model Cobalt-60 gamma cell obtainable at UKM.	50
Figure 3.11:	Linear accelerator (Elekta PRECISE) available at Department of Radiotherapy and Oncology, Pantai Hospital, Penang.	51
Figure 3.12:	Schematic diagram illustrating common features of TLD readers.	52
Figure 3.13:	Vacuum tweezers for picking up delicate lightweight materials.	53
Figure 3.14:	(Homogeneous mixture instrument) used in this study.	54
Figure 3.15:	Analytical balance (Presica XT 220A).	55
Figure 4.1:	XRD pattern of SiO <sub>2</sub> .	57
Figure 4.2:	XRD pattern of undoped compound (ZBS).	59
Figure 4.3:	XRD pattern of doped compound (ZBS:Cu <sub>2</sub> O).	60
Figure 4.4:	XRD pattern of codoped compound (ZBS:Cu.Sn).	60
Figure 4.5:	Plots of Differential Thermal Analysis of prepared sample.	62
Figure 4.6:	FESEM micrograph of (ZBS) glass sample.	63
Figure 4.7:	FESEM micrograph of (ZBS:Cu) glass sample	63
Figure 4.8:	FESEM micrograph of (ZBS:Cu.Sn) glass sample	64
Figure 4.9:	EDX emission of undoped (ZBS) glass.	65
Figure 4.10:	EDX emission of doped (ZBS:Cu) glass.	65
Figure 4.11:	EDX emission of codoped (ZBS:Cu.Sn) glass.	66
Figure 4.12:	The doped sample ZBS:Cu glow curve generated from 200 data points (irradiated by 50 Gy Cobalt-60).	69
Figure 4.13:	TL glow curve of pure ZBS glass.	70

Figure 4.14:	Difference of TL intensity with different concentrations of ZnO.	70
Figure 4.15:	Glow curves of ZBS:Cu with different concentrations of Cu <sub>2</sub> O doped.	72
Figure 4.16:	Difference of TL normalized intensity with diverse concentrations of Cu <sub>2</sub> O.	72
Figure 4.17:	Glow curves of ZBS:Cu.Sn with different concentrations of SnO <sub>2</sub> doped.	73
Figure 4.18:	Difference of normalized TL intensity with fixed Cu <sub>2</sub> O and diverse concentrations of SnO <sub>2</sub>	74
Figure 4.19:	Variation of (ZBS) TL intensity with annealing temperature.	75
Figure 4.20:	Variation of (ZBS) TL intensity with annealing time.	76
Figure 4.21:	Variation of (ZBS:Cu) TL intensity with annealing temperature.	76
Figure 4.22:	Variation of (ZBS:Cu) TL intensity with annealing time.	77
Figure 4.23:	Variation of (ZBS:Cu.Sn) TL intensity with annealing temperature.	78
Figure 4.24:	Variation of (ZBS:Cu.Sn) TL intensity with annealing time.	78
Figure 4.25	The co- doped sample ZBS:Cu.Snglow curve generated from 200 data points (irradiated by 50 Gy Cobalt-60).	80
Figure 4.26:	TL response of (ZBS) glass as a function of heating rate.	81
Figure 4.27:	Glow curve of (ZBS:Cu) glass as a function of heating rate.	81
Figure 4.28:	TL response of (ZBS:Cu) glass as a function of heating rate.	82
Figure 4.29:	TL response of (ZBS:Cu.Sn) as a function of heating rate.	83

Figure 4.30:	Comparison of dose response between ZBS, ZBS:Cu and ZBS:Cu.Sn at dose range 0.5-100 Gy irradiated by Cobalt-60 gamma ray.	85
Figure 4.31:	Compare dose response of glasses ZBS, ZBS:Cu and ZBS:Cu.Sn at dose range 0.5 - 4Gy 6 MeV.	86
Figure 4.32:	Compare dose response of glasses ZBS, ZBS:Cu and ZBS:Cu.Sn at dose range 0.5 - 4Gy 6 MV.	86
Figure 4.33:	Compare dose response of OPTIMUM glass sample ZBS:Cu.Sn and TLD 100 at dose range (0.5 – 4) Gy Cobalt -60.	87
Figure 4.34:	Compare dose response of OPTIMUM glass sample ZBS:Cu.Sn and TLD 100 at dose range (0.5-4.0) Gy 6 MeV.	88
Figure 4.35:	Compare dose response of OPTIMUM glass sample ZBS:Cu.Sn and TLD 100 at dose range (0.5-4.0) Gy 6 MV.	88
Figure 4.36	Dose response of OPTIMUM glass sample ZBS:Cu.Sn irradiated by different types of ionizing radiation.	89
Figure4.37:	Reproducibility of undoped ZBS glass samples irradiated with gamma ray Cobalt -60.	91
Figure4.38:	Reproducibility of doped ZBS:Cu glass samples irradiated with gamma ray Cobalt -60.	92
Figure4.39:	Reproducibility of codoped ZBS:Cu.Sn glass samples irradiated with gamma ray Cobalt -60.	92
Figure 4.40:	Fading characteristics of ZBSglass samples exposed to Co-gamma radiation.	94
Figure 4.41:	Fading characteristics of ZBS:Cuglass samples exposed to Co-gamma radiation.	95

Figure 4.42:	Fading characteristics of ZBS:Cu.Snglass samples exposed to Co-gamma radiation.	96
Figure 4.43:	Fading characteristics of ZBS, ZBS:Cu and ZBS:Cu.Sn glass exposed sun light.	97
Figure 4.44:	Fading characteristics of ZBS, ZBS:Cu and ZBS:Cu.Sn glass exposed fluorescent light.	98
Figure 4.45:	Geometric parameters of un-coped ZBS glow curve.	99
Figure 4.46:	Geometric parameters of coped ZBS:Cu glow curve.	100
Figure 4.47:	Geometric parameters of co-coped ZBS:Cu.Sn glow curve.	101
Figure 4.48:	Calculated energy dependence of undoped ZBS.	104
Figure 4.49:	Calculated energy dependence of doped ZBS:Cu.	106
Figure 4.50:	Calculated energy dependence of codoped ZBS:Cu.Sn.	107



## LIST OF ABBREVIATIONS

CB	Conduction band
DTA	Differential thermal analysis
EDX	Energy dispersive x-ray
ICRU	International commission of radiation units
LINAC	Linear accelerator
MDD	Minimum detectable dose
PMT	Photo-multiplier tube
RC	Recombination centre
RER	Relative energy response
SSD	Source surface distance
TL	Thermoluminescence
TLD	Thermoluminescence dosimeter
TLD100	Lithium fluoride dope with magnesium and titanium (LiF: Mg. Ti)
VB	Valance band
XRD	X-ray Diffraction
ZBS	Zinc borate silica
ZBS:Cu	Zinc borate silica doped with Cu <sub>2</sub> O
ZBS:Cu.Sn	Zinc borate silica codoped with SnO <sub>2</sub>

## LIST OF SYMBOLS

$\sigma_B$	Standard deviation
$\left(\frac{\mu_{en}}{\rho}\right)_m$	materials energy absorption coefficient
$\left(\frac{\mu_{en}}{\rho}\right)_{ref}$	reference material energy absorption coefficient
$\mu_g$	Symmetry factor
$a_i$	Fractional contents of electrons of element
$b$	Order kinetics
$B^*$	Mean thermoluminescence background signal
$B_2O_3$	Boron oxide
$C$	Coulomb
$Cu_2O$	Copper oxide I
$D$	Absorbed dose
$D(t)$	Radiation dose at time
$D_0$	Minimum detectable dose
$E_a$	Trap depth (activation energy)
$E_g$	Energy band gap
$F$	calibration factor
Gy	Gray
h	hour
$k$	Boltzmann's constant
$N_A$	Avogadro's number
min	Minute
$P$	Probability of trap electron
$S$	Frequency factor
s	Second
$S_E(E)$	Photon energy response
$S_i$	Sensitivity factor
$SiO_2$	Silica oxide
$SnO_2$	Tin oxide
T	Temperature

$t$	Time
$T_c$	Crystallization temperature
$T_g$	Transition temperature
$T_m$	Melting temperature
$W_i$	Weight fraction of element
$Z_{\text{eff}}$	Effective atomic number
$y$	year
ZnO	Zinc oxide

**PEMBANGUNAN KOMPOSIT BORON SILIKAT TAKTERDOP, TERDOP  
DAN KOTERDOP SEBAGAI DOSIMETER TERMOLUMINISEN UNTUK  
ARAS DOS PERTENGAHAN DAN TINGGI**

**ABSTRAK**

Kajian ini bertujuan untuk menilaikesan terdop dan koterdop keatas sifat sifat termoluminisens bagi sampel kaca zink borat silika (ZBS).Tiga jenis kaca disediakan dengan menggunakan kaedah tradisional, iaitu, teknik pencairan pelindapkejutan dan berasaskan kepada: komposisi takterdop (ZBS),  $(90-x)\text{ZnO}-x\text{B}_2\text{O}_3-10\text{SiO}_2$  yang mana  $x= 30, 35, 40, 45, 50$  mol%, komposisi terdop  $(45-x) \text{ZnO}-45\text{B}_2\text{O}_3-10\text{Si}_2\text{O}-x\text{Cu}_2\text{O}$  yang mana  $0.002 \leq x \leq 0.1\text{mol}\%$  dan komposisi koterdop  $(44.995-y)\text{ZnO}-45\text{B}_2\text{O}_3-10\text{Si}_2\text{O}-0.005\text{Cu}_2\text{O}-y\text{SnO}_2$  yang mana  $0.05 \leq y \leq 0.5\text{mol}\%$  telah dihasilkan. Nanopartikel  $\text{SnO}_2$  digunakan sebagai sampel kaca koterdop adalah bersaiz sekitar 22-31 nm. Semua sampel telah disahkan amorfus berdasarkan analisis belauan sinar-X. Kaca-kaca itu berada dalam keadaan haba stabil sebagaimana dapat ditentukan melalui analisis terma bezaan (DTA). Sampel berkenaan adalah tertakluk kepada jenis sinaran mengion yang berlainan seperti sinar gama Cobalt-60, elektron bertenaga tinggi 6 MeV dan foton sinar-x 6 MV. Sampel yang dicadangkan telah diradiasi dengan jenis sinaran mengion yang berlainan seperti sinar gama daripadadari Kobalt-60, 6 MeV elektron dan 6 MV foton sinar-x daripada LINAC. Untuk kaca ZBS takterdop, respon TL didapati sangat rendah berbanding dengan sampel terdop dan koterdop. Ini menunjukkan kesan terdop dan koterdop ke atas kaca tulen hos. Keamatan optimum TL juga direkodkan dengan kadar pemanasan 1 °C/s untuk Cu-terdop dan Sn koterdop. Walau bagaimanapun bagi sampel kaca hos, kadar pemanasannya adalah 3 °C/s. Rawatan haba pada 100 °C selama 15 min, 100

°C selama 30 min dan 300 °C selama 15 min telah diperoleh bagi sampel kaca takterdop, terdop dan koterdop masing-masing. Kepekatan optimum ZnO adalah 45 mol% untuk kaca tulen hos. Manakala, kepekatan optimum bagi Cu-terdop dan Sn koterdop adalah 0.005 mol% dan 0.1 mol% masing-masing. Lengkung bara tunggal dengan puncak ketara diperoleh pada 158 °C, 130 °C dan 147 °C bagi ZBS, ZBS:Cu dan ZBS:Cu.Sn, masing-masing. Keamatan TL bertambah baik bila hos kaca diterdop dan semakin bertambah baik dengan koterdop. Tiga jenis sampel kaca menunjukkan kelinearan dan pekali korelasi yang baik dalam julat dos sehingga 100 Gy Cobalt-60 dan julat dos 0.5-4.0 Gy elektron dan foton dari LINAC. Kepekaan dos dikesan minimum bertambah baik dengan sampel hos kaca (ZBS) terdop dan koterdop untuk semua jenis sinaran. Nombor atom berkesan yang tinggi diperoleh bagi kesemua sistem kaca. Nombor atom berkesan bagi ZBS, ZBS:Cu dan ZBS:Cu.Sn adalah 19.89, 19.96 dan 20.14, masing-masing. Tenaga pengaktifan bagi tiga sistem kaca ZBS, ZBS:Cu and ZBS:Cu.Sn adalah 0.819 eV, 0.873 eV dan 0.638 eV, masing-masing. Faktor frekuensi untuk ZBS, ZBS:Cu dan ZBS:Cu.Sn adalah  $2.33E+11 \text{ s}^{-1}$ ,  $4.70E+12 \text{ s}^{-1}$  dan  $2.65E+09 \text{ s}^{-1}$ , masing-masing. Semua komposisi kaca yang dicadangkan menunjukkan respon tenaga relatif foton yang lebih tinggi pada 0.04 MeV dan hampir tiada tindakbalas pada tenaga melebihi 0.1 MeV. Ciri-ciri TL untuk kaca itu dijelaskan secara terperinci, mengesahkan kemungkinan penggunaan sampel koterdop tersebut sebagai dosimetri TL untuk mengesan dan mengukur sinaran mengion.

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**ABSTRACT**

The aim of this study is to evaluate the impacts of doping and co-doping on the thermoluminescence properties of zinc borate silica (ZBS) glass samples. Three types of glasses were prepared by the traditional melt quenching technique: undoped composition  $(90-x)\text{ZnO}-x\text{B}_2\text{O}_3-10\text{SiO}_2$  where  $x= 30, 35, 40, 45, 50$  mol%, doped composition  $(45-x)\text{ZnO}-45\text{B}_2\text{O}_3-10\text{Si}_2\text{O}-x\text{Cu}_2\text{O}$  where  $0.002 \leq x \leq 0.1$  mol% and codoped composition  $(44.995-y)\text{ZnO}-45\text{B}_2\text{O}_3-10\text{Si}_2\text{O}-0.005\text{Cu}_2\text{O}-y\text{SnO}_2$  where  $0.05 \leq y \leq 0.5$  mol%. The size of the  $\text{SnO}_2$  nanoparticles used as codoped glass sample is around 22-31 nm. All the samples were confirmed to be amorphous using x-ray diffraction analysis. The glasses were found to be thermally stable as confirmed by differential thermal analysis (DTA). The proposed samples were irradiated to different types of ionizing radiation such as gamma ray from Cobalt-60, 6 MeV electrons and 6 MV x-ray photon from LINAC. For undoped ZBS glass, TL response was found to be very low compared with doped and codoped samples. This indicates the effect of doped and codoped on the pure host glass. The optimum TL intensity was recorded with a heating rate of  $1^\circ\text{C}/\text{s}$  for both Cu doped and Sn codoped, while for the host glass samples was  $3^\circ\text{C}/\text{s}$ . Thermal treatments at  $100^\circ\text{C}$  for 15 min,  $100^\circ\text{C}$  for 30 min and  $300^\circ\text{C}$  for 15 min were obtained for undoped, doped and codoped samples, respectively. The optimum concentration of ZnO was 45 mol% in pure glass host. Whilst, for both Cu doped and Sn codoped are 0.005 mol% and 0.1 mol%,

respectively. A single glow curve with a prominent peak was obtained at 158 °C, 130 °C and 147 °C for ZBS, ZBS:Cu and ZBS:Cu.Sn, respectively. The TL intensity was improved when the glass host was doped and further improved with codoped. Three types of glass samples showed good linearity and good correlation coefficient in a dose range of up to 100 Gy gamma ray from Cobalt-60 and dose range 0.5-4.0 Gy electron and photon from LINAC. The sensitivity and minimum detectable dose improved with the doped and codoped host (ZBS) glass samples for all types of radiations. High effective atomic numbers of glasses were found. ZBS, ZBS:Cu and ZBS:Cu.Sn have an effective atomic number of 19.89, 19.96 and 20.14, respectively. The activation energies of the three glass system are 0.819 eV, 0.873 eV and 0.638 eV for ZBS, ZBS:Cu and ZBS:Cu.Sn, respectively. The frequency factors for ZBS, ZBS:Cu and ZBS:Cu.Sn were found to be  $2.33\text{E}+11\text{ s}^{-1}$ ,  $4.70\text{E}+12\text{ s}^{-1}$  and  $2.65\text{E}+09\text{ s}^{-1}$ , respectively. All proposed compositions of glass reveal a higher photon relative energy response at 0.04 MeV and almost flat response at energies beyond 0.1 MeV. TL properties for present glasses are mentioned in details; supporting the possibility of using the proposed glasses sample as TL dosimetry for detecting and measuring ionizing radiations.

# CHAPTER1

## INTRODUCTION

### 1.1 Introduction

Dosimeters have been used as an important monitoring tool in personal and environmental monitoring in the field of medical research and radiation therapy. Every day humans are being exposed to radiation sources, especially the people who work in radiation areas such as nuclear energy plants and hospitals where they may induce genetic defects and cancer. There is a lot of public awareness of radiation dosimetry, hence people are looking for alternative ways of obtaining personal and environmental dosimeters.

Nowadays different types of dosimeters are used for measuring absorbed doses and these include film, ionization chambers, semiconductor dosimeters (e.g. diodes), thermoluminescent dosimeters, alanine and gel. Whereas some of these dosimeters are reusable such as ionization chamber, thermoluminescent dosimeters (TLDs), diode, others are not (films, gels etc). These dosimeters need to be calibrated from time to time to ensure their consistency.

Thermoluminescent dosimeters are crystalline materials that store absorbed energy inside their structure from exposure to ionizing radiation and release this absorbed energy as visible light when it is heated ((Podgorsak, 2005). Thermoluminescent dosimetry is used in many scientific and applied fields. TL dosimeters are small in size and therefore they are easy to handle and can be used feasibly as personnel dosimeters.



Some other uses of TL dosimeters include radiation protection, radiotherapy clinic, industry, and environmental and space research, using many different materials (Shani, 2000).

TLDs have been developed significantly over the years and a lot of materials were studied to see if they were suitable for applications in different areas for dosimetry (McKinlay, 1981). TL materials store energy inside their structure when they are irradiated, as electrons and holes are caught in trapping centres because of defects. When that material is heated, electrons and holes recombine at luminescence centres, and thus light is emitted. The light is measured using a photomultiplier tube (PMT) inside the reader device.

Many factors have to be taken into account in order to find the most suitable material. The availability is very important as well as the stability of its produced signal. A low fading rate is important (lower than 5% per month) as well as simple glow curves with a plain anneal heating cycle. The sensitivity of TLD can be increased by adding impurities called activators. As there are more impurities in the material, more traps are included and thus more light is emitted during thermoluminescence process. Therefore the efficiency of the material is increased (Knoll, 2010).

The use of the thermoluminescence (TL) technique in radiation dosimetry becomes popular after the launch of lithium fluoride by Daniels and his colleagues (Daniels et al., 1953). Daniels and his group first suggested the use of thermal stimulate luminescence (TSL) as a technique in radiation dosimetry.

Through their studies Lithium fluoride was earlier used to measure radiation dose after a bomb test. Soon the idea of using TSL in dosimetry caught on and many groups started working in the field of thermoluminescent dosimetry (TLD).

## **1.2 Statement of the Problem**

Studies of thermoluminescent materials have been extended to glasses, nanoparticles and optical fibers. The application of thermoluminescent technology has also been developed in the food preservation field. This shows that the use of TLD is not restricted to personal and environmental monitoring alone but has also been developed for use in the food industry.

There are a lot of new compounds produced by researchers, but none of them have all the desired properties such as near tissue equivalence, high sensitivity, excellent stability and a simple glow curve structure. The latter properties ideally sought are a single glow peak at about 200 °C, and a simple annealing procedure for reproducibility. So, there have always been efforts made to either prepare new dosimetric materials with enhanced thermoluminescence characteristics or just to improve upon the already existing dosimetric materials by varying the concentration of impurities or by codoping of the phosphor with other elements or doping new impurities in new matrices. Lately, investigations of thermoluminescence dosimetry in glass as a new material have been carried out. Among these new materials are the Borate glasses. There are many researchers who work on borate glasses modified by several elements; however, investigations on borate silica's thermoluminescence TL properties have not been studied.

### **1.3 Objectives of the research**

The objectives of the research are:

- a) To produce a high quality of the  $\text{SiO}_2$  using free raw rice husk and use it as one of materials in glass formation.
- b) To determine the optimum TL characteristics for undoped (ZBS) as a host and optimising dopant and codopant concentrations in this host.
- c) To determine the best setting of the annealing procedure and heating rate of the undoped, doped and codoped compositions under study.
- d) To investigate the fundamental thermoluminescence properties when undoped, doped and codoped of ZBS are irradiated to Cobalt-60 gamma ray, 6 MeV electrons and 6 MV x-ray photons.
- e) To compare and calibrate the optimum glass sample under study with standard glass phosphor TLD 100 and to ensure similarity of properties between the optimum sample under study and standard TLD 100.

### **1.4 Scope of the research**

This research will focus on undoped, doped and codoped zinc borate silica glass systems for thermoluminescence dosimeter purposes. In order to study the characteristics of new materials, the samples will be analysed using field emission scanning electron microscopy (FESEM), x-ray diffraction (XRD) and differential thermal analysis (DTA). Three types of glass samples undoped, doped and codoped ZBS will be irradiated using a linear accelerator machine (LINAC) at 6 MeV electron and 6 MV x-ray photon beams and Cobalt-60 gamma ray in order to study the linearity, sensitivity and minimum detectable dose of the new materials.

Irradiation by gamma ray Cobalt-60 will be used to study optimization, time temperature profile, annealing procedure, and analyze the glow curve of undoped, doped and codoped glass samples.

### **1.5 Outline of thesis**

Chapter one covers the background of the study and its research problem. This chapter also includes the suggestions and research questions, planned objectives, the scope of study and the outline of the thesis.

Literature review related to this study is presented in chapter two. The general notion of luminescence and thermoluminescence in particular, in addition to the theories and models related with thermoluminescence are integrated in this chapter. The dosimetric properties of thermoluminescent phosphor and some previous work are also discussed.

Explaining methods and procedures as well as the instrumentation involved in this work is presented in chapter three. The methods and procedures include the identification of materials and the glass sample preparation. Methods and procedures with regard to thermoluminescence studies are also described in this chapter.

The results obtained from the characterization, temperature time profile settings and optimization of undoped, doped and codoped compositions and the main dosimetric properties of the proposed TLDs are discussed in chapter four.

Chapter five includes the summary of the findings of the work. Conclusion and recommendations for future work are also included.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

In this chapter, the discussion will focus on the hypothesis of thermoluminescence phenomena and the dosimetric properties of thermoluminescence. Three essential ingredients for the production of thermoluminescence; first, second and general order kinetics will also be explained. Methods to analyze TL glow peaks and determine various parameters such as the trap depths ( $E_a$ ) and the frequency factors ( $S$ ) will be determined. Earlier works related to this study will also be discussed.

#### 2.2 Luminescence

When a material is irradiated by ionizing radiation, some of the incident photons energy will be absorbed by the electrons and then emitted as a photon with a longer wavelength in the visible region of the electromagnetic spectrum, this process is called luminescence. Thermoluminescence is a type of luminescence caused by heating the material and the result is light emission (McKeever, 1988, Chen and McKeever, 1997). The main types of luminescence are fluorescence and phosphorescence.

##### 2.2.1 Fluorescence

In fluorescence, the electrons return to ground state immediately after excitation with released light as shown in Figure 2.1a. The mean time between these transitions is between  $10^{-3}$ s -  $10^{-8}$  s.

## 2.2.2 Phosphorescence

Figure 2.1b illustrates the type of luminescence where electrons are trapped and then belatedly return to ground state. The transition of electrons to ground state is forbidden, they need energy to move. In this luminescence process the excited electron is captured in a localized state at metastable level and then released into a state excited level, where it acquires energy  $\Delta E$  ( $E_e - E_m$ ). The electron will, as a result, relax to a ground state  $g$ , thus emitting light. If  $\tau_c > 10^{-8}$  s is between excitation and emission then the trapping process causes a longer delay. The mean time of an electron to stay in a trap at temperature  $T$  is given by Equation (2.1).

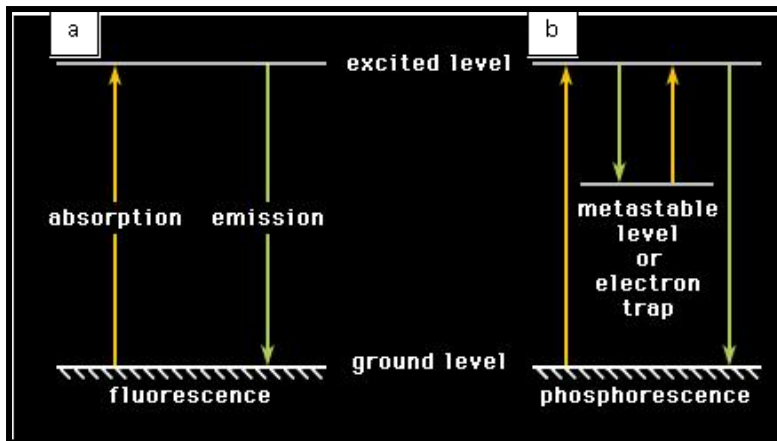


Figure 2.1: Electron transitions involve in the processes of (a) fluorescence (b) Phosphorescence.

$$\tau = S^{-1} \exp\left(\frac{E}{KT}\right) \quad (2.1)$$

where  $S$  is the frequency factor,  $E$  is the trap depth (the energy difference between trap level and conduction band),  $k$  is the (Boltzmann's constant= $8.617 \times 10^{-5}$  eV/K) and  $T$  is temperature in Kelvin. The luminescence process that takes place in

this way is called phosphorescence. Phosphorescence is therefore temperature dependent.

### 2.2.3 Model of thermoluminescence

Each TL material possesses scheme of energy band. The general model is the one used to explain the basic features of thermoluminescence, this model includes only two localized state, trap centre (E) and recombination centre (L) as shown in Figure 2.2. After exposure to ionizing radiation, there are three stages in the process of producing TL in a material. These are electrons trapping, holes trapping and the recombination of electrons and holes.

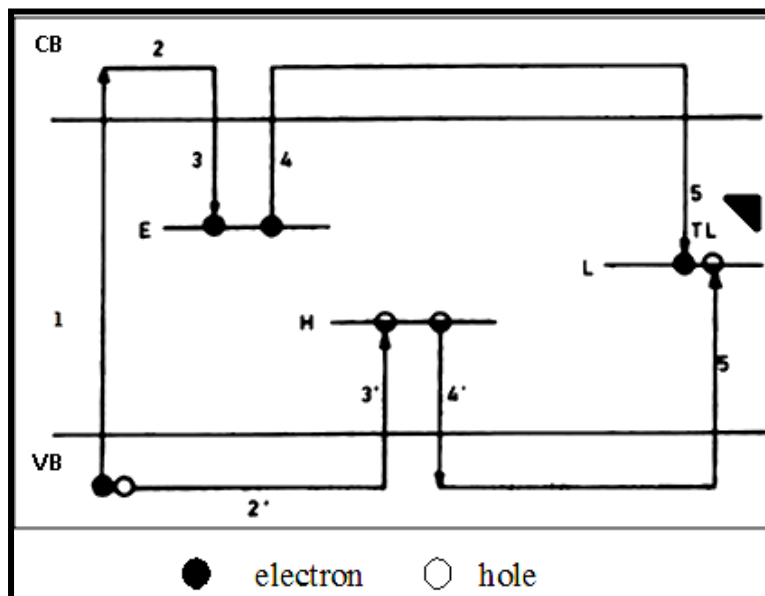


Figure 2.2: A simple energy band model for thermoluminescence (McKinlay, 1981).

Figure 2.2 shows the energy band pattern of each stage. Free electrons are created and moved to the conduction band after the substance has absorbed energy during irradiation with ionizing radiation (step 1). Free electrons can move through the crystal or amorphous system (step 2). In a place where there are trapping levels such as E (metastable state) the electron may become trapped in this trap (step 3).

The holes left due to ionization from the valence band may also migrate via the valence band (step 2'). These holes may also be trapped (step 3'). But hole centers are very unstable and can easily decay rapidly at room temperature (step 4'). The captured electrons will remain in the traps until they have acquired sufficient energy to escape. Electrons staying in traps is a function of two factors; the depth of the trap and the temperature of the material. Therefore raising the temperature of the material will give the trapped electrons enough energy to be released (step 4). Luminescence centers such as L, serve as recombination centers where electrons and holes recombine and release excess energy as visible light or ultraviolet photons (step 5). With the introduction of a modifier, dopant and codopant, there will be a creation of additional traps and recombination centers. TL emission will therefore be enhanced (Attix, 2008). The probability  $P$  of the escape of the electron from a metastable state to an excited state is given by Boltzmann equation.

$$P = 1/\tau = S \exp\left(-\frac{E}{KT}\right) \quad (2.2)$$

The exponential factor  $\exp\left(-\frac{E}{KT}\right)$  is the probability of an electron escaping when it encounters with thermal energy. If  $E > KT$ , a trapped electron will stay in the trap level  $E$ . After irradiation, there will be a considerable population ( $n$ ) of electrons in the trap level. On the other hand, there must be the same population of holes at level  $H$  because the free electrons and holes are produced in pairs and annihilated in pairs (recombination center). This population of electrons and holes show a non equilibrium state due to the normal equilibrium Fermi level  $E_f$ , where  $E_f$  is situated lower than  $E$  level and higher than  $H$  level.

The return to equilibrium can be faster by rising the temperature of the samples above  $T_0$  such as  $E \leq KT$ . By heating the sample, the probability of de-trapping  $P$



will be increased and the electrons will now be freed from the trap and shift into the conduction band. Consequently free electrons will recombine with the holes and the outcome is thermoluminescence. The glow peak is analyzed by an empirical method in which a parameter called the order of kinetics is introduced.

### **2.3 Glow curve theory**

A typical glow curve shows one or more glow peaks. Every peak indicates information about each trap level and the state of occupation in the TL material. The orders of kinetics obtained by an empirical method analysis of the glow peak, the thermal energy cause the trapped electrons to jump into the conduction band; they have two kinds of chance to jump down. One is the re-trapping process of returning to the same kind of traps and the other is recombination with the hole which is accompanied by the emission of TL light (Alam and Bauk, 2010).

#### **2.3.1 First order kinetics**

In 1945 Randall and Wilkins proposed an arithmetical expression for a TL peak in a glow curve. The analysis for an isolated glow peak is based on electrons being trapped at a discrete energy level below the conduction band; during heating of sample, the electrons are thermally released from the traps, and then recombine with holes at recombination centers as shown in Figure 2.2. The probability of re-trapping is negligible (Randall and Wilkins, 1945). Thus, According to this model, the TL intensity  $I$ , at a constant temperature can be written as

$$I_{(t)} = -\frac{dn}{dt} \tag{2.3}$$

where  $n$  is the concentration of trapped electrons at time  $t$ .

The recombination rate of free electrons is equal to the releasing rate of trapped electrons. The intensity of thermoluminescence,  $I_{(t)}$  equals the recombination rate of free electrons, which yields.

$$I_{(t)} = -\frac{dn_h}{dt} = -\frac{dn}{dt} = nS \exp\left(-\frac{E}{KT}\right) \quad (2.4)$$

where  $n_h$  is the concentration of holes in the recombination center. If the heating rate is constant, it can be shown as a simple linear heating function:  
 $T = T_0 + \beta T$ .

When the material is heated at constant rate of temperature  $\beta = \frac{dT}{dt}$  ( $k \cdot s^{-1}$ ), then the solution of Eq. (2.4) is

$$\frac{dn}{n} = -\left(\frac{S}{\beta}\right) \exp\left(-\frac{E}{KT}\right) dT \quad (2.5)$$

On integration of equation (2.5)

$$n(T) = n_0 \exp\left\{-\left(\frac{S}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{KT'}\right) dT'\right\} \quad (2.6)$$

where  $n_0$  is the initial concentration of electrons in the trap populated at the starting heating temperature  $T_0$  (k). The temperature dependence of the emitted TL is given by:

$$I(T) = n_0 S \exp\left(-\frac{E}{kT}\right) \exp\left\{-\left(\frac{S}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{KT'}\right) dT'\right\} \quad (2.7)$$

This equation described the thermoluminescence process with first order kinetics (Kitis et al., 1998).

### 2.3.2 Second order kinetics

Garlick and Gibson preferred not to suppose that re-trapping was negligible; in this case the trap filling process may be described as:

$$I(t) = -\frac{dn}{dt} = \frac{n^2}{N} S \exp\left(-\frac{E}{KT}\right) \quad (2.8)$$

where  $n$  is the concentration of electrons in the conduction band;  $N$  is the concentration of an available electron trap of depth  $E$  below the conduction band (Garlick and Gibson, 1948).

Taking into account that  $dt = \frac{dT}{\beta}$ , the luminescence intensity of irradiated phosphor under an increasing temperature is obtained in the following way

$$\frac{dn}{n^2} = \frac{S}{N\beta} \exp\left(-\frac{E}{KT}\right) dT \quad (2.9)$$

By integrating

$$\int_{n_o}^n \frac{dn}{n^2} = -\frac{S}{N\beta} \int_{T_o}^T \exp\left(-\frac{E}{KT}\right) dT \quad (2.10)$$

$$\frac{1}{n_o} - \frac{1}{n} = -\frac{S}{N\beta} \int_{T_o}^T \exp\left(-\frac{E}{KT}\right) dT \quad (2.11)$$

$$n = n_o \left\{ 1 + \left(\frac{S}{N\beta}\right) \int_{T_o}^T \exp\left(-\frac{E}{KT}\right) dT \right\}^{-1} \quad (2.12)$$

Then, the equation describing the TL intensity for second order is given by:

$$I(T) = \frac{n_o^2 S \exp\left(-\frac{E}{KT}\right)}{N \left\{ 1 + \left(\frac{n_o S}{N\beta}\right) \int_{T_o}^T \exp\left(-\frac{E}{KT'}\right) dT' \right\}^2} \quad (2.13)$$

### 2.3.3 General order kinetic

May and Partridge (1964) have suggested an empirical equation to explain the TL glow peak when conditions for neither first-order nor second order are convinced . This is known as the general order kinetics equation and its deferential form has been suggested and it covers several cases (Rasheedy, 1993, McKeever and Chen, 1997, Sunta et al., 1999, Alam and Bauk, 2010).

$$I(t) = -\frac{dn}{dt} = \frac{Sn^b}{N^{b-1}} \exp\left(-\frac{E}{KT}\right) \quad (2.14)$$

where b is the order of kinetics. Generally the value of b is supposed to be between 1 and 2, but sometimes it can exceed this range. The solution of Eq 2.14 is given below for  $b \neq 1$

$$I(T) = \frac{S''n_o \exp\left(-\frac{E}{KT}\right)}{\left\{1 + \frac{S''(b-1)}{\beta} \int_{T_o}^T \exp\left(-\frac{E}{KT'}\right) dT'\right\}^{\frac{b}{b-1}}} \quad (2.15)$$

where  $S'' = S\left(\frac{n_o}{N}\right)^{b-1}$

### 2.4 Applications of the thermoluminescence

Radiation dosimetry was among the different applications of thermoluminescence as suggested by Daniel and his colleagues (Danial et al., 1953). Absorbed energy results in electron-hole pair production and filling of metastable states when a sample is exposed to ionizing radiation. The energy stored in the sample is proportional to the TL intensity. The early material employed to serve as a TL dosimeter behind atomic weapon tests in the 1950's was Lithium fluoride LiF (McKeever, 1985). TL application has continued to expand since that time. The innovation and improvement of instrumentation has helped utilize TLD phosphor in

various fields (McKeever, 1988) There are three main areas using TL as reported by (Pekpak et al., 2010) which are archaeological aging, geological dating and radiation dosimetry.

Many studies have been made regarding the phenomenon of TL. They studied the TL mechanism for pure and impure materials in basic research (Mesterházy et al., 2012, Gastéllum et al., 2002).

## **2.5 TLD characteristic and measurement**

Thermoluminescence has been used for several years as a technique for radiation dosimetry, particularly in ionizing irradiation. However, not all known materials are appropriate for dosimetry or tissue equivalent. TL materials are divided into two main groups (Rivera, 2012):

- a) Materials that are tissue equivalent, and that show poor sensitivity to ionizing radiation.
- b) Materials with a high sensitivity to ionizing radiation but with a high effective atomic number (not tissue equivalent).

The important characteristics of thermoluminescence dosimetry are annealing procedure, glow curve, sensitivity, dose response, reproducibility, and stability and fading.

### **2.5.1 Annealing procedure**

The heat treatment is a process done before irradiation, which is considered an important parameter for the removal of the effects of the preceding irradiation (Prokic, 2001). Consequently the results of measurement will be exact for the dose applied through irradiation (Pekpak et al., 2010). This process starts with thermal treatment by putting the TLDs glass samples in an oven and heating them to a predetermined temperature, maintaining the heating at that temperature for a predetermined time and then cooling it down to room temperature (Bos, 2001).

For every TL material utilized in dosimetric applications, it is significant to know the procedure for returning its basic conditions after an irradiation. This process is the annealing procedure and it has two goals:

- a) To empty the traps of the phosphor completely after the irradiation and readout cycle.
- b) To settle down the electron traps in order to obtain, within narrow limits, the same glow curves even after repeated irradiation and thermal treatments.

Different annealing is necessary in order to blank all the traps (shallow and deep) of the phosphor. Numerous TL materials also possess different peaks at a low temperature; these peaks are likely to be emptied even at room temperature, so in many cases it is required to carry out a partial annealing before the reading in order to minimize noise in the information. This procedure is known as pre-read annealing (Horowitz et al., 2001).

### **2.5.2 Glow curve**

The area under the curve is called the glow curve, the area under the glow curve signifies the radiation energy deposited (Pradhan and Bhatt, 1981). The curve can be a plot of the luminescent light yield or intensity against temperature. The glow curve is a good indicator for identifying if the materials are suitable for thermoluminescence. Ideally, that the glow curve gives a peak at around 200 °C, with a single and simple peak. If the peak is observed at a low temperature around 100 °C and is fading away quickly, the information about the radiation content cannot be yielded. Also a peak is not assigned to good TL properties when it is observed at around 300 °C (Hunda et al., 2005). There are some parameters that affect the shape, size and position of the glow curve in every readout case. These parameters are the heating rate, radiation dose, activator used and the annealing procedure (Pradhan and Bhatt, 1981). The preparation of the concentration of and the basic chemical used have an influence over the intensity and the glow curve. Peak temperatures and shapes are also affected by doping methods and synthesis (Prokic, 2001, Kayhan and Yilmaz, 2011).

### **2.5.3 Glow curve analysis**

There are various methods for analyzing the glow curve to evaluate TL parameters, for instance activation energy  $E_a$ , frequency factor  $S$  and the order of kinetics  $b$ . These some of TL parameters evaluation methods (Furetta and Weng, 1998):

- a) Methods based on the analysis of the glow curve shape.
- b) Methods based on the temperature at the maximum.
- c) Initial Rise Method.

- d) Area measurement method.
- e) Method based on the various Heating Rates.
- f) Isothermal method.
- g) Inflection method.
- h) Numerical curve fitting methods.

Randall and Wilkins (1945) pioneered the glow curve analysis, and then followed by Garlick and Gibson (1948) who established that the initial rising part of the TL curve was exponentially dependent on temperature. The trapping parameters of a TL material consist of kinetic order  $b$ , frequency factor  $S$  and activation energy  $E_a$ . A peak shape method has been proposed by (Chen and Winer, 1970).

### 2.5.3.1 Chen's Method

General TL glow curve and the parameters in the peak shape glow curve analysis methods are shown in Figure 2.3. The shape method glow curve for TL analysis was developed more generally by Chen in 1969 (Aboud, 2013), who considered both first and second order kinetics. Then the activation energy becomes:

$$E_\alpha = C_\alpha \left( \frac{kT_m^2}{\alpha} \right) - b_\alpha (2kT_m) \quad (2.16)$$

$$\tau = (T_m - T_1), \quad \delta = (T_2 - T_m), \quad \omega = (T_2 - T_1). \quad (2.17)$$

where  $\alpha$  is a factor, that depends on the glow curve temperature widths,  $b_\alpha$  is a constant that depends on the order of kinetics and the glow curve temperature widths. The  $C_\alpha$  is also a constant that depends on the order of kinetics and glow curve



temperature widths (McKeever, 1988). The values of  $C_\alpha$  and  $b_\alpha$  for the first and second orders are shown in Table 2.1.

The geometric factor can as well serve as for determining whether recombination process of a phosphor is first or second order kinetic. The values for geometric factors  $\mu_g$  expressed by equation (2.18) and summarized as:

$$\mu_g = 0.42 \quad \text{For first order}$$

$$\mu_g = 0.52 \quad \text{For second order}$$

$$\mu_B = \frac{T_2 - T_m}{T_2 - T_1} \quad (2.18)$$

Table 2.1: Values for the constants  $C_\alpha$  and  $b_\alpha$

	First order			Second order		
	$\tau$	$\delta$	$\omega$	$\tau$	$\delta$	$\omega$
$C_\alpha$	1.51	0.976	2.52	1.81	1.71	3.54
$b_\alpha$	1.58	0	1	2	0	1

Chen (1997) established an expression for general order kinetics. It is dependent on the geometric factors of the glow peak as:

$$C_\tau = 1.510 + 3.0(\mu_g - 0.42) \quad (2.19)$$

$$b_\tau = 1.58 + 4.2(\mu_g - 0.42) \quad (2.20)$$

On the other hand, if  $\delta$  is used

$$C_\delta = 0.976 + 7.3(\mu_g - 0.42) \quad (2.21)$$

and  $b_\delta = 0$

In the case in which  $\omega$  is used,

$$C_\omega = 2.52 + 10.2(\mu_g - 0.42) \quad (2.22)$$

and  $b_\omega = 1$

The above terms for C's and b's are applicable for cases where the frequency factor is only weakly dependant on temperature. The frequency factor S can be calculated once the activation energy is obtained using the following equation.

$$S = \left(\frac{\beta}{T_m^2}\right) \left(\frac{E}{k}\right) * \frac{1}{1+(b-1)\left(\frac{2kT_m}{E}\right)} \exp\left(\frac{E}{kT_m}\right) \quad (2.23)$$

where  $\beta$  is the linear heating rate,  $b$  is the order of kinetics,  $E$  is the activation energy and  $T_m$  is the max temperature.

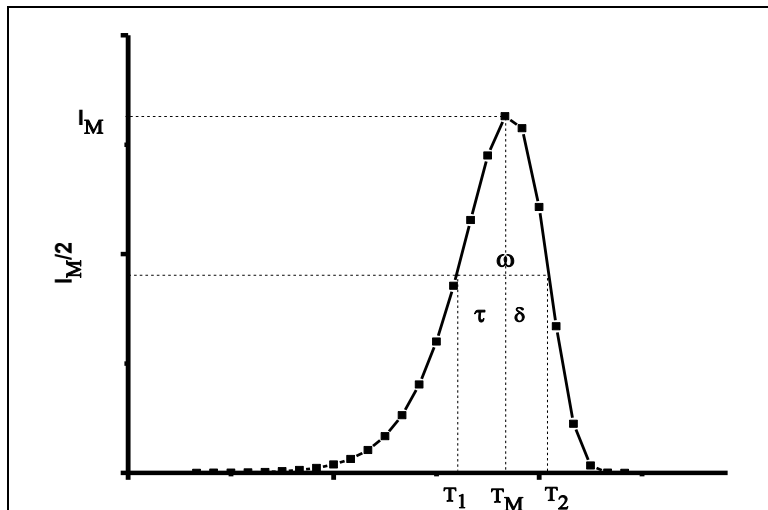


Figure 2.3: General TL glow curve, showing also the parameters discussed in the peak shape glow curve analysis methods.

#### 2.5.4 Sensitivity

The glow curve area ( $TL$ ) per unit mass of the dosimeter ( $m$ ) and per unit of dose ( $D$ ) in unit ( $nC\ g^{-1}\ Gy^{-1}$ ) is called the TL sensitivity as shown in equation 2.24, (Furetta et al., 2000).

$$S(D) = \frac{TL}{m \cdot D} \quad (2.24)$$

This data is given relatively to the TL sensitivity of TLD-100 (McKeever et al., 1995), then:

$$R(D) = \frac{S(D)_{material}}{S(D)_{TLD-100}} \quad (2.25)$$

The TL sensitivity depends on both TL materials and reader system, for instance the heating profile and light detection system (Rasid, 2015). Dosimeters from the same production batch might be different in their sensitivity. Different reasons may account for the differences of the sensitivity of the same dosimetric material such as: difference in the detectors masses; difference in the optical density of the detectors; or contamination that may cover the surface of a detector. The calibration process, known as Elemental Correlation Coefficient (ECC) between dosimeters of the same batch can minimized the error by 1-2% (Bøtter-Jensen et al., 2003).

#### 2.5.5 Dose response (linearity)

The linear relation between TL intensity ( $I$ ) and the absorbed dose ( $D$ ) is an important characteristic of a TL dosimeter. Some TL materials show non-linear

escalation at the range of dose of interest. However, the sign of non-linear regions in the dose response curve of a TLD is not sufficient reason to ignore its use as a TLD, it only means that it needs good calibration and correction (McKeever, 1988, Pekpak et al., 2010). The plot of the TL response as a function of various doses may demonstrate different zones. This can be seen in Figure 2.4 where the TL emission is not linear in the low dose  $D_1$  region and also at high dose  $D_s$ . Two universal indices have been suggested to describe all forms of nonlinearity. First is called superlinearity index where it shows the indication of change in the slop of the dose response. Second is known as supralinearity index or dose function where it is used to quantify the size of the correction needed for extrapolation of the linear dose region.

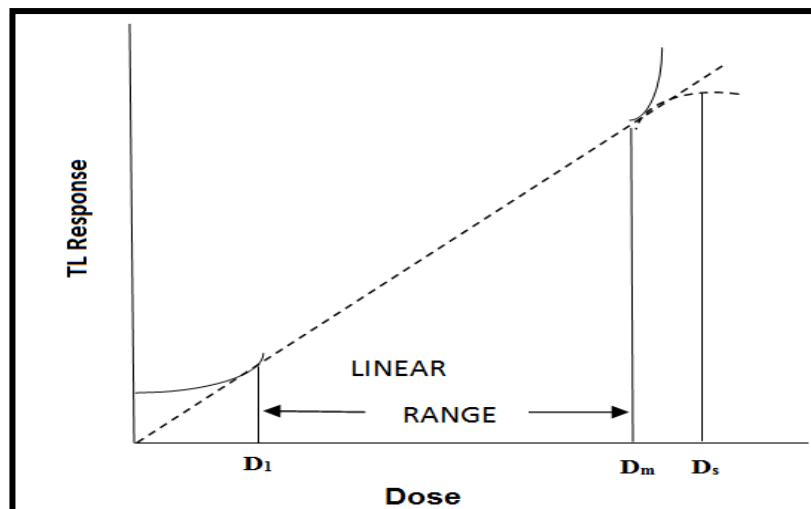


Figure 2.4: The various zones which could be observed in a plot of TL as a function of dose (Furetta, & Weng, 1998).

A fundamental relation between TL response and the absorbed dose can be given as the equation (2.26):

$$y = ax + b \quad (2.26)$$