# SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ZINC DOPED $MgB_4O_7$ BASED GLASS THERMOLUMINESCENCE DOSIMETER FOR RADIOTHERAPY AND INDUSTRIAL APPLICATIONS

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by

**MUHAMMAD BAKHSH**

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| | |
|---|---|
| $\gamma$ | Gamma |
| $^{o}C$ | Degree Celsius |
| µGy | Micro Gray |
| Ag | Silver |
| a.u | Arbitrary Unit |
| BC | Before Christ |
| BO | Boron Oxide |
| $B_2O_3$ | Borate |
| Ca | Calcium |
| CB | Conduction Band |
| Ce | Cerium |
| cGy | Centi Gray |
| Co | Cobalt |
| Cs | Caesium |
| Cu | Copper |
| $D_{max}$ | Maximum depth |
| DSC | Differential Scanning Calorimetry |
| Dy | Dysprosium |
| EDX | Energy Dispersive X-ray |
| Er | Erbium |
| ER | Energy Response |
| ENDO | Endothermic |

| | |
|---|---|
| Eu | Europium |
| eV | Electron Volt |
| EXO | Exothermic |
| FESEM | Field Emission Scanning Electron Microscopy |
| FWHM | Full Width at Half Maximum |
| Gd | Gadolinium |
| Gy | Gray |
| IEC | International Electrotechnical Commission |
| IMRT | Intensity Modulated Radiation Therapy |
| IR | Initial Rise |
| K | Potassium |
| KERMA | Kinetic Energy Released per unit Mass |
| keV | Kilo Electron Volt |
| kV | Kilo Volt |
| LET | Linear Energy Transfer |
| LINAC | Linear Accelerator |
| $Li_2O$ | Lithium Oxide |
| LiF | Lithium Fluoride |
| Ln | Lanthanides |
| mA | Milli Ampere |
| MB | Magnesium Borate |
| MDD | Minimum Detectable Dose |
| MeV | Mega Electron Volt |

| | |
|---|---|
| Mg | Magnesium |
| $MgB_4O_7$ | Magnesium Borate |
| mGy | Milli Gray |
| MgO | Magnesium Oxide |
| Mn | Manganese |
| MOSFET | Metal Oxide Semiconductor Field Effect Transistor |
| Mol% | Mole Percent |
| MV | Mega Volt |
| Na | Sodium |
| nC | Nano Coulomb |
| Nd | Neodymium |
| nm | Nano meter |
| OAR | Organ at Risk |
| OSL | Optically Stimulated Light |
| PM | Photomultiplier |
| PMT | Photomultiplier Tube |
| Pr | Praseodymium |
| PS | Peak Shape |
| RER | Relative Energy Response |
| Sm | Samarium |
| Sr | Strontium |
| SSDL | Secondary Standard Dosimetry Laboratory |
| SD | Standard Deviation |

| | |
|---|---|
| SSD | Source to Surface Distance |
| Tb | Terbium |
| $T_c$ | Crystallization Temperature |
| $T_g$ | Glass Transition Temperature |
| Ti | Titanium |
| TL | Thermoluminescence |
| TLD | Thermoluminescence Dosimeter |
| $T_m$ | Maximum Temperature |
| TTP | Time Temperature Profile |
| VB | Valance Band |
| UV | Ultraviolet |
| XRD | X-ray Diffraction |
| Y | Yttrium |
| Yb | Ytterbium |
| $Z_{eff}$ | Effective Atomic Number |
| Zn | Zinc |
| ZnO | Zinc Oxide |

# SINTESIS, PENCIRIAN DAN PENILAIAN DOSIMETER TERMOPENDARCAHAYA KACA ASAS $MgB_4O_7$ UNTUK JAMINAN KUALITI DI DALAM APLIKASI RADIOTERPI DAN INDUSTRI

## ABSTRAK

Kajian ini bertujuan untuk membangunkan dosimeter termopendarcahaya (TL) yang amat sensitif dan setara tisu untuk jaminan kualiti dalam teknik radioterapi moden dan aplikasi industri. Siri kaca $MgB_4O_7$, dengan komposisi X(MgO) - 100-X($B_2O_3$) di mana $35 \leq X \leq 45$ mol%, Magnesium Borat (MB), X(ZnO) - 35-X(MgO) - 65($B_2O_3$) $0 \leq X \leq 1$ mol%, Zink didopkan Magnesium Borat (MB: Zn) dan X($Li_2O$) - 0.4(ZnO) - 35- X (MgO) - 65($B_2O_3$) di mana $0 \leq X \leq 0.1$ mol% Magnesium Borate didop Zink didop bersama Litium (MB: Zn, Li) telah disintesis dengan menggunakan kaedah konvensional pelindapan lebur. Keadaan amorfus sampel yang disintesis telah dianalisis melalui pembelauan sinar-X (XRD) dan seterusnya disahkan dengan Mikroskop Elektron Pengimbas Medan Pancaran (FESEM). Kaca dengan komposisi terpilih menunjukkan kebolehan pembentukan kaca yang baik, kaca $MgB_4O_7$, 0.56, kaca $MgB_4O_7$:ZnO, 0.61 dan kaca $MgB_4O_7$:ZnO,$Li_2O$, 0.56. Tambahan pula, siri kaca yang disintesiskan didapati mempunyai kestabilan kaca yang baik, dengan kaca $MgB_4O_7$, 1.73, kaca $MgB_4O_7$:ZnO, 1.62 dan kaca $MgB_4O_7$:ZnO,$Li_2O$, 0.76. Keluk cahaya bagi kaca MB (35 mol%) mendedahkan satu puncak dosimetrik yang utama pada suhu maksimum ($T_m$) 200 °C. Peneguhan dalam tindak balas TL dengan faktor 1.46 dengan anjakan puncak dosimetrik ke arah suhu yang lebih tinggi, 240 °C, diperhatikan dengan pengenalan ZnO (0.4%) sebagai dopan dalam matriks kaca MB yang membentuk MB: Zn. Peningkatan selanjutnya dalam balas tindak TL diperhatikan oleh faktor 1.16 dengan anjakan puncak dosimetrik ke arah suhu yang lebih tinggi pada 250 °C, dengan menambahkan $Li_2O$ sebagai dopan bersama dalam matriks kaca MB yang membentuk MB:Zn,Li. MB:Zn,Li mempunyai bilangan atom yang hampir setara tisu ($Z_{eff}$ = 8.87) menunjukkan kelinearan yang sangat baik sehingga 5 kGy dengan balas tindak TL yang lebih tinggi berbanding dengan MB dan MB:Zn. Kestabilan isyarat yang baik dengan 10% kepudaran selama tempoh dua minggu untuk MB: Zn,Li berbanding 15% untuk MB: Zn dan 20% untuk MB. However, optical fading results suggest that dosimeters must be stored on a light tight environment. Namun, keputusan pudaran optik mencadangkan bahawa dosimeter-dosimeter ini perlu disimpan di dalam persekitaran kedap cahaya. Sebagai kesimpulan, kaca MB:Zn,Li mempunyai potensi untuk digunakan sebagai TLD untuk jaminan kualiti dalam teknik radioterapi moden.

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## ABSTRACT

The present study is aimed to develop a highly sensitive and tissue equivalent thermoluminescent dosimeter for quality assurance in modern radiotherapy techniques and industrial applications. Series of $MgB_4O_7$ glasses, of compositions X(MgO) - 100-X($B_2O_3$) where $35 \leq X \leq 45$ mol%, Magnesium Borate (MB), X(ZnO) - 35-X(MgO) - 65($B_2O_3$) where $0.1 \leq X \leq 1$ mol%, Zinc doped Magnesium Borate (MB:Zn) and X($Li_2O$) - 0.4(ZnO) - 35- X (MgO) - 65($B_2O_3$) where $0.01 \leq X \leq 0.1$ mol%, Lithium co-doped Zinc doped Magnesium Borate (MB:Zn, Li) are synthesized using conventional melt-quenching method. The amorphous nature of synthesized samples is analysed through X-ray diffraction (XRD) and further confirmed with Field Emission Scanning Electron Microscopy (FESEM). The selected glass compositions demonstrated good glass forming abilities, $MgB_4O_7$ glass, 0.56, $MgB_4O_7$:ZnO glass, 0.61 and $MgB_4O_7$:ZnO,$Li_2O$ glass, 0.56. Moreover, the synthesized glass series are found to have good glass stabilities, $MgB_4O_7$ glass, 1.73, $MgB_4O_7$:ZnO glass, 1.62 and $MgB_4O_7$:ZnO,$Li_2O$ glass, 0.76. The glow curve of MB glass with 35 mol% of MgO revealed a single prominent dosimetric peak at a maximum peak temperature ($T_m$) of 200 $^oC$. An enhancement in TL response by a factor of 1.46, with a shift in dosimetric peak towards higher temperature at 240 $^oC$, is observed with introduction of ZnO (0.4%) as a dopant in MB glass matrix forming MB:Zn. Further enhancement in TL response is observed by a factor of 1.16 with a shift in dosimetric peak towards higher temperature at 250 $^oC$ by adding $Li_2O$ as co-dopant in MB glass matrix forming

MB:Zn,Li. MB:Zn,Li having nearly tissue equivalent effective atomic number, $Z_{eff} = 8.87$, showed excellent linearity up to 5 kGy with higher TL response as compared to MB as well as MB:Zn. MB:Zn,Li has good signal stability with 10% fading over a period of two weeks for as compared to 15% for MB:Zn and 20% for MB. However, optical fading results suggest that dosimeters must be stored on a light tight environment. In conclusion, MB;Zn,Li glass has potential to be used as TLD for quality assurance in modern radiotherapy techniques as well as in industrial radiation dosimetry applications.

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

Humans are being exposed to ionizing radiations in their daily life whether intentionally or unintentionally. The health risks associated with the exposure to these radiations are minimal until and unless they are within the safe limits, set by national or international regularity authorities. Radiation dosimeters plays vital role in radiation dosimetry and radiation protection as they provide valuable dosimetric information which helps the regularity authorities to monitor and assure the radiation safety. However, the efficiency of a radiation dosimeter is always questionable depending upon its application, especially in mixed radiation fields.

Engström *et al.* (2005); Podgorsak (2005) defined a radiation dosimeter as a device, instrument or system that measures or evaluates the radiation quantities i.e. absorbed dose or equivalent dose, KERMA, exposure, either directly or indirectly. Desirably, a dosimeter is characterized by its accuracy and precision, dose rate or dose dependency, linearity, energy response, directional dependency and spatial resolution. Obviously, not all dosimeters can satisfy all characteristics. Therefore, the radiation dosimetry system can be selected by judiciously taking account the radiation environment.

Most commonly available commercial radiation dosimeters are Ionization chamber, MOSFET, Film dosimeter, Thermoluminescence (TL) dosimeter and survey meters. These radiation dosimeters are divided in to two categories active dosimeters and passive dosimeters. Active dosimeters provide instant information regarding the radiation dose, Ionization chamber, MOSFET and survey meters fall under this category. Whereas on the other hand passive dosimeters require some time to produce dosimetric information. Film dosimeter and Thermoluminescence dosimeter are categorized as passive dosimeters. The significant advantage of passive dosimeters over active dosimeters is their ability to retain the dosimetric information which can be extracted later when required. The radiation dosimeter for proposed application is critically selected by looking over at different aspects of the requirements and conditions.

Thermoluminescent dosimeters and film dosimeters are being used in environmental radiation monitoring, personal dosimetry as well as quality assurance in modern radiotherapy techniques. Though, both dosimeters are passive dosimeters having some merits and demerits. The prominent advantage of thermoluminescence dosimeters over film dosimeters is their reusability, which is considerably important in developing countries due to their limited financial resources. On the other hand, the main disadvantage of thermoluminescent dosimeter is the loss of dosimetric information with time and storage conditions, which can be overcome by developing new TL material with improved fading properties.

The basic aim of radiotherapy is to deliver maximum radiation dose to the target volume without over exposing surrounding normal tissues to avoid long term complications. Accurate and precise dose measurement is essential to optimize treatment out comes. The necessity of efficient dosimetric tools has been significantly increased due to hypo fractionated radiation dose in modern radiotherapy techniques which improves the quality of the treatment. The treatment quality is significantly important to get desirable treatment outcomes in radiotherapy. However, due to treatment cast it is quite difficult to provide quality treatment with limited financial resources in developing countries. Pre-treatment dose assessment is of great importance in modern radiotherapy techniques due to its legal importance as well which requires highly sensitive dosimeters.

All the passive dosimeters are capable of dose recording but thermoluminescence dosimeter (TLD) is an economically feasible passive dosimeter due to its reusability. A thermoluminescence dosimeter (TLD) has potential to be used as radiation dosimeter in radiation therapy because of its small size, near tissue equivalent properties and capability of point dose measurements to optimize treatment quality to achieve the proposed radiotherapy goal. It can be used for in vivo dosimetry on patients, either for routine quality assurance procedure or dose monitoring in special cases i.e. dose to organs at risk, complex geometries, total body irradiation, brachytherapy. TL dosimeters are also useful for treatment technique verification in various phantoms. TLDs can be used for postal dosimetry audits Podgorsak (2005).

Thermoluminescence as radiation dosimetry technique was first introduced by Farrington Daniels and his co-researchers in 1953 for medical radiation dosimetry S. W. S. McKeever *et al.* (1995). A thermoluminescent dosimeter (TLD), for its use in clinical dosimetry, is evaluated based on its sensitivity (to X-rays, γ-rays, electrons and neutrons), accuracy, precision, dose response, effective atomic number ($Z_{eff}$), reproducibility, glow curve structure and fading. An extremely sensitive TLD with high spatial resolution and reproducibility is desirable for precise absorbed dose measurements.

Uncertainties in constituent concentrations give rise to uncertainties in detailed parameters of thermoluminescence process, resulting in variations in the TL glow peak temperature, TL efficiency, light intensity as well as emission spectra. The growth of

TLD materials is governed by the laws of thermodynamics which leads to unavoidable uncertainties regarding the incorporation of impurities. The thermoluminescence properties are critically dependent upon the defect structure, therefore, the variation in defect structures caused by these statistical thermodynamic effects results in undesirable variations in TL properties. The uncertainties in the concentration gives rise to corresponding uncertainties that results in variations in the TL glow peak temperatures, light intensity, the emission spectra and the efficiency of the thermoluminescence. Due to this chaos nature of the TL material it is impossible to predict the behaviour of even a single TLD chip of the same batch S. W. S. McKeever *et al.* (1995). The sensitivity of any thermoluminescence dosimetry system is strongly interdependent of light emitted by TL material and sensitivity of the reader to that light. To develop a highly sensitive TL dosimetry system either the TL material should emit light within the sensitive range of the light detector or the light detector should be sensitive to the light emitted from the TL material.

The most widely used commercial TL dosimeters, for X-ray and γ-ray dosimetry, i.e. are TLD-100 and TLD-600. However, these dosimeters are used in low level radiation detection due to the low-level saturation limit. Though TLD-100 shows good sensitivity at low radiation levels but has complex annealing procedure and low linear dose range Furetta (2003).

A newly developed TL material should demonstrate several dosimetric properties, i.e. high sensitivity, good linearity, low fading, low energy dependence, good reproducibility and simple TL glow curve to be considered as an alternative TL dosimeter. Intensive research has been carried out to overcome these drawbacks by different researchers. Schulman *et al.* (1967) introduced a new TL material by replacing fluoride with borate. The proposed material was doped with MnO and produced in crystalline form which resulted in improved effective atomic number ($Z_{eff}$ = 7.3) but showed lower radiation sensitivity. This disadvantage was attributed to the incompatibility between the light emitted (600 nm) by TL material and the photomultiplier tube response of the TL reader to the emitted light. The sensitivity was significantly enhanced by Kazanskaya and his team Kazanskaya *et al.* (1974) by replacing lithium with magnesium. The newly developed phosphor was activated with dysprosium oxide which shifted the luminescence light to shorter wavelengths (475 and 580 nm) which match the photomultiplier tube (PMT) sensitive region at the cast of effective atomic number which increased to 8.4. The phosphor was synthesized in polycrystalline form. The glow curve was observed to have a single dosimetric peak between 190 $^{o}$C to 200 $^{o}$C. The sensitivity is reported to be 10 to 20 times higher than the standard TLD-100 with linear dose response from $10^{-5}$ to 10 Gy. Thermal fading is reported to be ~ 25% over a storage time of 40 days. The dose linearity range was improved up to 102 Gy Barbina *et al.* (1981); M. Prokić (1980). However, high variability of the TL properties within a batch as well as between different batches was reported by different researchers Barbina *et al.* (1981); Driscoll *et al.* (1981) suggesting the need of improvement of material synthesization to utilize such a phosphor extensively in personnel and environmental dosimetry without individual detector calibration. Furetta and his team reported improved TL properties of $MgB_4O_7$ when activated with Dysprosium and co-activated with Sodium. They reported different relative sensitivities for same TL material when measurements were acquired with different TLD readers which confirms the interdependency of light emitted from TL material and PMT sensitivity. The $MgB_4O_7$:Dy,Na TL dosimeters are used for legal personal dosimetry on large scale in Yugoslavia Furetta *et al.* (2000).

## 1.2 Problem Statement

Due to complexity of dose distribution in modern radiotherapy treatment techniques the severity of associated risk increases with increasing the treatment dose. In vivo dosimetry is a suitable dosimetry technique to minimize such risk and to enhance the treatment quality. Due to the small size, compatibility and cost efficiency thermoluminescence dosimeters (TLDs) are suitable of in vivo dosimetry. Ideally, TL dosimeters should be tissue equivalent with excellent sensitivity. Unfortunately, even for most commonly used TL materials either one of the desirable characteristic is compromised i.e. LiF:Mg,Ti, $Li_2B_4O_7$ doped with Cu or Mn impurities or $Be_2O_3$ doped with different impurities are considered to be tissue equivalent but demonstrate poor sensitivity on the other hand, highly sensitive TL materials i.e. $CaF_2$ doped with Mn, Dy or Tm impurities or $CaSO_4$ doped with Mn or Tm impurities compromises on tissue equivalency. Though LiF:Cu,Mg,P phosphor (TLD-100H) possess improved TL properties as compared to LiF:Mg,Ti (TLD-100) but still demonstrates some disadvantages i.e. complex glow curve and greater sensitivity to heating procedures as compared to TLD-100. Moreover, annealing of TLD-100H above 240 $^{o}$C results in an irreversible sensitivity loss by altering the glow curve which leads to high residual dose. The LiF: Mg,Cu,P (TLD-100H) and LiF:Mg,Ti (TLD-100) have small linear dose range of 10 Gy and 1 Gy, respectively. The dosimeters demonstrates approximately identical energy response above 100 KeV, however, TLD-100 over-respond at low energy X-rays, whereas, TLD-100H under respond at same energies Ben-Shachar (1999). The dose response of highly sensitive LiF:Mg,Cu,P as well as $Al_2O_3$:C TL materials decreases with increasing ionization density of the radiation field which could lead in underestimation of the dose upon heavy charged particle irradiation Olko (2010). Furthermore, the most widely used commercial TL dosimeters i.e. Lithium Fluoride family, TLD-100, TLD-600 and TLD-700, have complex preparation methods Furetta (2003). Teixeira reported dose response of TLD-200, TLD-400 and TLD-800. The dosimeters were reported to have a linear dose range from 0.1 Gy to 10 Gy for TLD-200 and from 1 Gy to 100 Gy for TLD-400 and TLD-800, respectively, when exposed to Co-60 γ-rays Teixeira *et al.* (2008). Moreover, careful handling of currently available TLD powders is another restriction for postal radiation dosimetry audits using TLDs Mizuno *et al.* (2008). The $MgB_4O_7$ TL dosimeters are highly sensitive with acceptable thermal fading and are reported to be practically in use for legal personal dosimetry in Yugoslavia Furetta *et al.* (2000). The reported disadvantage of $MgB_4O_7$ TL dosimeter is its sensitivity to light which results in optical fading. Moreover, the $MgB_4O_7$ TL dosimeters are also of hygroscopic nature which results in loss of sensitivity as well as batch variation. The linear dose range was identified to be up to 75 Gy. Annalakshmi *et al.* (2013) reported $MgB_4O_7$: Gd,Li polycrystalline powder prepared by solid state sintering technique is five times more sensitive than the standard TLD-100, when irradiated to 83 Gy which is out of therapeutic range.

## 1.3 Research Objectives

The core object of this research is to develop a highly sensitive glass-based tissue equivalent thermoluminescence dosimeter for clinical and industrial radiation dosimetry. The specific objectives to achieve the core objective of this study are:

1. To synthesis highly sensitive tissue equivalent $MgB_4O_7$, $MgB_4O_7$:Zn, $MgB_4O_7$:Zn,Li glass based TL dosimeters
2. To characterize the physical properties of the newly developed glass based dosimeters

3. To optimize TL dosimetric characteristics of newly developed glass-based TL dosimeters
4. To evaluate the dosimetric properties of the newly developed glass based thermoluminescence dosimeter (TLD) for photon beams

## 1.4 Scope of Research

Magnesium Borates are attractive thermoluminescence dosimeter hosts due to their attractive dosimetric properties i.e. tissue equivalency, high sensitivity to external radiation dose, good linearity and simple glow curve. Moreover, the cost efficiency is another noticeable advantage due to its chemical constituents. This research is focused on development of a glass based highly sensitive tissue equivalent thermoluminescence dosimeter as the glass dosimeters shows minimal fading and are easy in handling. In this study, three series of glass dosimeters ($MgB_4O_7$, $MgB_4O_7$:Zn, $MgB_4O_7$:Zn,Li) are synthesized using conventional melt quenching method. The synthesized glass samples are characterized and evaluated on dosimetric basis targeting the therapeutic dose range. This study is an effort to optimize the feasibility of $MgB_4O_7$ based glass thermoluminescence dosimeter.

## 1.5 Research Significance

The newly developed magnesium borate glass based thermoluminescence dosimeters expand the limitations of thermoluminescence dosimetry. The newly developed thermoluminescence dosimeter with improved dosimetric characteristics allows the user to select a single dosimeter for a wide range of radiation dosimetric applications. Moreover, present study will provide an insight into the feasibility of glass-based dosimeters in medical radiation dosimetry, personal radiation dosimetry, dosimetry audits, industrial radiation dosimetry as well as accidental radiation dosimetry. In addition, the findings of this research could provide an alternative TL dosimeter for in vivo dosimetry to improve the treatment quality by enhancing the dose to the target volume and reducing the dose to the surrounding critical organs.

## 1.6 Thesis Design

This thesis consists of five chapters including chapter 1; An introductory chapter which introduces with the research background which leads to research problem identification alternatively identifying the scope of the research by giving an idea about the significance of the research. Chapter 2 contains empirical and theoretical framework for current study based on latest literature. It introduces with the radiation dosimeter paying special focus on thermoluminescence dosimeter, its characteristics and requirements depending on the field of application. In addition, recent developments and achievements in $MgB_4O_7$ based TL dosimeters are discussed. A thorough overview of borate glasses is also given in this chapter. Chapter 3 includes the materials and methods used to accomplish the proposed objectives of this study. The findings of this study are presented and discussed in chapter 4. The study is concluded in chapter 5 with identified future directions.

# CHAPTER 2

# LITERATURE REVIE

## 2.1 Introduction

This chapter introduces with radiation dosimeters mainly focusing on thermoluminescence dosimeters and their significance for personal radiation dose monitoring as well as medical radiation dosimetry including in vivo dosimetry in modern radiotherapy techniques. Moreover, an overview about the properties and characteristics of glass and magnesium borate glass is presented here. In addition, $MgB_4O_7$ based TL dosimeters are also discussed in detail. The significance of proposed TL dosimeter is briefly discussed based on latest findings by different researchers in the field.

## 2.2 Radiation Dosimeter

A radiation dosimeter is a device that measures, either directly or indirectly, the dosimetric quantities like absorbed dose or equivalent dose and KERMA of ionizing radiation. A radiation dosimetry system consists on a set of radiation dosimeter along with the reader interfaced through dedicated software. The accuracy and precision, linearity, dose and dose rate dependence, directional dependence and spatial resolution are desirable properties for a dosimeter to be used in radiotherapy Podgorsak (2005). The active dosimeters have advantages of producing real time dose measurements over passive dosimeters. However, passive dosimeters have remarkable advantage of storing dosimetric information, over active dosimeters.

## 2.3 Thermoluminescent Dosimeter

Some materials, upon irradiation, absorb energy and retain part of the absorbed energy in metastable states. When this energy is subsequently released in the form of ultraviolet, visible or infrared light, the phenomenon is known as luminescence. The luminescence phenomenon is classified in to two categories fluorescence and phosphorescence, depending on the time delay between stimulation and the emission of light. Fluorescence occurs with a time delay $10^{-10} \leq T \leq 10^{-8}$ Sec whereas phosphorescence occurs with a time delay, $T < 10^{-8}$ Sec. Moreover, suitable excitation source accelerates the phosphorescence process which further categories the luminescence process depending on the excitation source. The phenomenon is referred as optically stimulated luminescence (OSL) if the excitation source is light. The phenomenon is referred as thermoluminescence if the excitation source is heat.

Ideally, a thermoluminescence phosphor should contain high trap concentration with a high efficiency of light emission associated with recombination process. Fading is one of the major issues associated with most of the newly developed TL materials. An acceptable stability of trapped charges, as storage time and storage temperature function, is desirable for minimum fading. Ideally, a TL material must emit light spectrum between wavelength 300 nm to 500 nm since it corresponds to commercially available detector systems. Beside that the glow curve should be simple for easy interpretation of the readings to avoid any post irradiation thermal treatment. The peak temperature at the maximum of the main dosimetric peak is desirable in the temperature range of 180 $^{o}$C to 250 $^{o}$C. Furthermore, the TL material should not suffer from radiation damage in the dose range of application. Tissue equivalent TL materials are required to have minimum photon energy dependence in personal and medical radiation dosimetry application. Non-toxicity is another important factor for in vivo dosimetry in medical radiation dosimetry. A wide linear dose range is desirable for a good TL material. In radiotherapy dose rate and irradiation angle independent TL response is highly required. The lower detection limit is of great importance in environmental radiation dosimetry so a TL material with minimum lower detection limit is appreciated. Low self-irradiation, due to natural radionuclides in TL materials, is desirable for accurately estimate the dose.

## 2.4 Characteristics of Thermoluminescent Dosimeter

### 2.4.1 Batch Homogeneity

A group of TLDs with same chemical composition with identical irradiation as well as thermal background that are produced at the same time under similar synthesization conditions is termed as a batch of TLDs. Whereas, homogeneity is a behavioural condition under which TLDs are supposed to produce more or less similar results.

Homogeneity between newly synthesized TLD batches is of major concern due to its importance in large scale dosimetric applications, where individual calibration is not applied, i.e. environmental radiation monitoring and personal radiation dose monitoring. Though International Electrotechnical Committee (IEC) has set a standard tolerance limit, for personal dosimetry, to accept or reject the TL dosimeter the batch homogeneity is still a user dependent characteristic of the TLD. The batch homogeneity is identified by user by setting tolerance limits depending on the field of application. The extended tolerance limit, i.e. 20-30% to mean response, introduces significant precision error in the dose estimation which is potentially risky when dosimeters are applied in modern radiotherapy techniques. As high precision is required for dose measurement in clinical radiation dosimetry, the dosimeter response can be corrected by applying individual calibration factor based on calibration exposures. Though it is a user dependent characteristic, the synthesization method is also of great importance as the batch homogeneity is highly influenced by synthesization method. The batch homogeneity can vary significantly, for the identified tolerance limits, depending upon the synthesis method Furetta (2003); Furetta *et al.* (1998); M. Oberhofer *et al.* (1981). The batch homogeneity can be determined through uniformity test which can be expressed as follow Furetta (2003);

$$\Delta_{max} = \frac{(M-M_o)_{max}-(M-M_o)_{min}}{(M-M_o)_{min}} \times 100 \leq 30 \tag{2.1}$$

where $M$ represents TL response of exposed sample, to a test dose, and $M_o$ represents background TL reading of annealed but unexposed sample. The TLDs causing the linearity index, $\Delta_{\max}$, out of tolerance limit should be rejected. Another procedure can be adopted to check the batch homogeneity by evaluating the average value of all TL measurements as follow Furetta (2003);

$$\bar{M} = \sum_{i=1}^{N} \frac{(M_i-M_{oi})}{N} \tag{2.2}$$

The TLDs exhibiting TL reading out of tolerance limit, $\bar{M} \pm \sigma_p$ should be rejected.

### 2.4.2 Glow Curve

The graphical representation of the luminescence intensity, I, as a function of the temperature, T, is termed as glow curve. A glow curve may consist of several TL peaks representing different trapping levels, resulting from different impurities. These peaks may or may not be resolved in glow curve Furetta (2003). The emission spectrum is the spectral energy distribution of the TL light that is emitted and forms the glow peaks. The height of the peak, or the area under the glow curve, may be used as a measure of the absorbed dose in the phosphor. When the peak height is utilized measure exposure or absorbed dose, the heating cycle must be closely reproducible to avoid peak height variation Mahesh *et al.* (1989). The glow curve shape is dependent on several controllable and uncontrollable parameters, i.e. the nature and amount of impurity presented in TL material, the type of radiation, the amount of absorbed dose, heating rate applied during sample readout, previous thermal treatment including cooling rate, nonradiation induced signals from the TL reader as well as TL material and the accumulated absorbed dose.

For some materials the glow peak temperature shifts to higher temperatures with increasing heating rate, while glow peak height decreases due to thermal quenching. Therefore, it is required to optimize the heating rate for any newly developed dosimeter. Therefore, the heating rate should be specified when representing a glow curve. At higher heating rates, the glow peaks may overlap due to thermal lag. The glow curve recording is of great benefit in routine dosimetry measurements, as it can be helpful in detecting instrumental malfunctions, i.e. improper thermal contact between the heating medium and the dosimeter or anomalous appearance of nonradiation induced signals. A lower integration limit, when integrating the glow curve, can exclude low temperature peaks that contribute to the fading. A low temperature plateau can provide optimal separation of the low and high temperature peaks. An upper integration limit is of significant value to exclude, at least to some extent, non-radiation-induced signals resulting from the TL dosimeter or TLD reader.

### 2.4.3 Annealing (Thermal treatment)

Annealing is the thermal treatment applied to a TL material either to sensitise the TL material or reduce the thermal fading. The annealing is classified into two categories; Pre-irradiation annealing and post irradiation annealing. Pre-irradiation annealing is required to erase any irradiation history by erasing the residual signal completely without damaging the dosimetric material. Annealing for extended periods at higher temperatures significantly reduces the sensitivity M. Oberhofer *et al.* (1981). Therefore, it is necessary to optimize the annealing parameters to sensitise the newly developed TL material. The appropriate annealing procedure will sensitize the TL material by stabilizing the holes and traps. Generally speaking, high temperature annealing is needed to clear the dosimetric traps of residual signal which may cause unwanted background during subsequent use of TL dosimeter. The TL response of any TL dosimetric material strongly depends on annealing procedure applied. Every TL dosimetric material has its own optimum annealing procedure. The optimum annealing procedure, for a TL dosimeter, is a combination of annealing temperature and annealing time to obtain highest TL response with lowest standard deviation with acceptable reproducibility. The reproducible cooling rate is highly desirable as the sensitivity of the TL dosimetric material is greatly influenced by cooling rate adopted to cool down the TL material to room temperature after annealing at predetermined temperature for set time M. Oberhofer *et al.* (1981). Every TL dosimetric material has its own annealing parameters due to its unique chemical composition. A simple annealing procedure is desirable for an economically efficient TL dosimetry system. The standard annealing, for LiF:Mg,Ti, consists of high temperature thermal treatment at 400 $^{o}$C for 1 hour followed by a low temperature thermal treatment at 100 $^{o}$C for 2 hours or 80 °C for 20 hours which is considered to be complex annealing procedure Furetta (2003).

The primary purpose of post irradiation low temperature annealing is to remove any low temperature glow peaks ≤100 °C that are thermally unstable at room temperature which could contribute to the thermal fading of the TL material. The annealing optimization procedure for post irradiation is same as that of pre-irradiation the only difference is the annealing temperature as for post irradiation annealing the TL material is subjected to temperatures less than that of dosimetric peak temperature whereas for pre-irradiation annealing the TL material is subjected to higher temperatures.

### 2.4.4 Time Temperature Profile (TTP)

It is a user defined set up which extracts the dosimetric information from the TL dosimeter. The time temperature profile (TTP) controls the thermal treatment of the TL material by controlling different parameters i.e. heating rate applied during readout, the pre-heat temperature and the maximum temperature to which the dosimetric information needs to be extracted. Therefore, the acquisition time varies depending upon the thermal treatment applied. The time temperature profile (TTP) varies depending upon chemical composition of the TL material alternatively affecting the glow curve of the TL material. Therefore, it is recommended to optimize the glow curve setting prior to start TL measurements for any newly developed TL material.

### 2.4.5 Effective Atomic Number ($Z_{eff}$)

Dosimetric materials with effective atomic number, $Z_{eff}$, resembling to that of human tissue ($Z_{eff}$ =7.4) are said to be tissue-equivalent materials. Tissue equivalence is the most desirable dosimetric features of any TL dosimetric material for personal and medical radiation dosimetry. It is a desirable dosimetric feature for accurate measurements. Tissue equivalence is of great importance for radiological dosimetry, where photoelectric interaction is predominant up to photon energy of 100 keV. Thus, the TL dosimeters with high effective atomic numbers are highly sensitive to photon energies below 100 keV A. Bos (2001); Furetta (2003). The cross-sections for photon interactions are directly proportional to the atomic number, Z, raised to some numerical power for each element in the dosimeter material, i.e.: elemental cross-section α $Z^x$, where $x$ depends on the type of interaction occurring and varies between 1 and 5. Its value has been reported to be 2.94 or 3.75 for photoelectric effect. A compound, as a thermoluminescent material is, may be regarded as a single element with an effective atomic number, $Z_{\text{eff}}$ , given by Khan *et al.* (2014):

$$Z_{eff} = \sqrt[m]{\sum_i a_i Z_i^m} \qquad (2.3)$$

Where $a_i$ is the fractional electron content of $i^{th}$ element of the compound.

### 2.4.6 Sensitivity

Sensitivity is considered as one of the most significant dosimetric feature of a TLD material. The sensitivity of a TLD material may be expressed, in general, as the TL response, in reader units, per unit of dose and unit of mass of the sample Furetta (2003). The sensitivity can be calculated as;

$$S = \frac{TL}{D.m} \qquad (2.4)$$

where $TL$ is the thermoluminescence response, $D$ is the test dose and $m$ is the weight of the sample.

Absolute sensitivity is influenced by many factors including TL reader used for measurements, optical filters, heating rate, optical density of the sample, dirt contamination of the sample surface as well as concentration and type of dopant. Due to the uncertainties associated with the absolute measurements of sensitivity McKeever and colleagues introduced the term relative sensitivity which allows to compare the TL signal from material of interest with the TL signal from LiF:Mg,Ti (TLD-100), given by S. W. McKeever *et al.* (1995);

$$S(D)_r = \frac{S(D)_{TLD\ material}}{S(D)_{TLD-100}} \tag{2.5}$$

### 2.4.7 Energy Response

The energy response is the variation of the detected TL output, for a fixed dose, as a function of the energy of the absorbed radiation. This variation stems from the dependence of the material's absorption coefficient on radiation energy S. W. McKeever *et al.* (1995). Low $Z_{eff}$ materials are preferred since the most desirable response is flat. A newly developed TL dosimeter must be evaluated based on energy response before its recommendation for dosimetric application. Normally air and tissue are considered as reference materials, therefore a TL material with effective atomic number, $Z_{eff}$, equals to tissue will demonstrate a good energy response. The direct measurements for energy response is obtained when the material is under electronic equilibrium conditions M. Oberhofer *et al.* (1981). The energy response of any TL material must be well known to evaluate its dosimetric application. The energy response or energy dependence is the measure of the energy absorbed in the thermoluminescence material in comparison to the energy absorbed in a reference material (i.e. air or human tissue) when irradiated at same radiation dose. The energy response is the characteristic of TL material itself. The response of high effective atomic number materials will be higher in low energy range (20 keV - 100 keV) due to dominancy of photoelectric effect. The energy response is ratio between mass energy absorption coefficients of TLD material and the reference material based on Bragg principle for large cavities given by, S. W. S. McKeever (1985);

$$S(E) = \frac{\left(\frac{\mu_{en}}{\rho}\right)_{TLD}}{\left(\frac{\mu_{en}}{\rho}\right)_{ref}} \tag{2.6}$$

Air is usually used as medium of reference as it is well defined quantity for which exposure can be precisely measured as well as the ratio between absorbed dose and exposure is constant. The energy response calculation has significant meaning up to 3 MeV. However, in practice, the energy response calculation for high energies does not have any significance due to absence of electronic equilibrium Martin Oberhofer *et al.* (1981).

The energy response of $MgB_4O_7$ doped with Dy and Tm when normalized to Co-60 is 1.5 whereas the energy response normalized to Cs-137 is between 1.3 to 2.4. Normally Co-60 (1.25 MeV) is considered as reference photon source therefore, it is convenient to introduce the relative energy response, RER, of the thermoluminescence dosimetric material, at the photon energy E, normalized to the Co-60 energy, given by Furetta (2003);

$$RER = \frac{S(E)}{S(E)_{Co_{60}}} \tag{2.7}$$

Generally, the energy response of a thermoluminescent dosimeter at a specified energy is normalized to Co-60. Ideally, the response of dosimeters should be energy independent. However, practically, if a dosimeter demonstrates a small alteration with photon energy the energy response of the dosimeter can be considered as good. Energy response of a dosimeter is strongly effective atomic number, $Z_{eff}$ dependent. The dosimetric materials having low effective atomic number, $Z_{eff}$, demonstrate constant energy response over the energy range of interest.

As TLD material is a compound of various elements, additivity rule should be applied to determine the mass energy absorption coefficients;

$$\left(\frac{\mu_{en}}{\rho}\right)_{TLD} = \sum_i \left(\frac{\mu_{en}}{\rho}\right)_i . W_i \tag{2.8}$$

where $\left(\frac{\mu_{en}}{\rho}\right)_i$ is mass energy absorption coefficient of element and $W_i$ is fractional weight of $i^{th}$ element.

### 2.4.8 Dose Response

The functional dependency of measured TL intensity on absorbed dose is termed as dose response. Ideally, a dosimetric material should demonstrate linear dose response over a broad dose range. Whereas, practically a TLD material demonstrate linear, then supralinear and then sublinear behaviour with increasing the dose A. Bos (2001); S. W. McKeever *et al.* (1995). Linear dose range of a TLD material can be determined through supralinearity index given as;

$$f(d) = \frac{F(d)/d}{F\ (d_0)/d_o} \tag{2.9}$$

where $F(d)$ is the dose response at a dose $d$ and $d_o$ is a lower dose where dose response is linear. Thus, ideal TL dosimeter would satisfy $f(d) = 1$ over a wide dose range to demonstrate linear behaviour. The dosimeter behaviour is said to be supralinear, over estimation of the dose, if $f(d) > 1$ whereas $f(d) < 1$ demonstrate sublinear behaviour, under estimation of the dose S. W. McKeever *et al.* (1995).

Supralinearity, a function of the linear energy transfer (LET) of interacting radiation and the dose where supralinearity can be clearly evident, increases with increasing LET of the radiation. The TL dosimeters must be annealed properly, in order to restore its previous sensitivity, if once irradiated in supralinearity range before subsequent re-use. The upper dose limit for each detector is determined by saturation effect which is set to be 20% below saturation value M. Oberhofer *et al.* (1981). The linear dose range requirement for radiotherapy is identified between $10^{-1}$ - $10^{2}$ A. Bos (2001).

### 2.4.9 Fading

The fading is a statistical phenomenon in which holes and electrons are released from their traps and consequently recombined through thermal and optical stimulation. Fading is an unwanted characteristic of thermoluminescence material, specifically in environmental radiation dosimetry, due to complex stimulating factors that are difficult to control in natural environment. The probability of fading phenomena is a function of temperature, given by M. Oberhofer *et al.* (1981);

$$P = S\,exp^{(-E/kT)} \tag{2.10}$$

where $P$ is probability of transition, $S$ is frequency factor, $E$ is activation energy, $k$ is Boltzmann's constant and $T$ represents absolute temperature. Equation 2.10 shows the interdependency of fading behaviour on the frequency factor $S$, trap depth $E$ and absolute temperature $T$. The time required by trapped electrons decrease to half of their initial population is termed as glow peak half-life, given by

$$\tau = 0.693P^{-1} \tag{2.11}$$

where $P$ represents probability of transition.

Ideally, TL material should demonstrate no signal loss at room temperature; however if it demonstrates minimal fading the material would be said to have good stability Kamil (2011). The maximum peak temperature ranging from 200 °C to 250 °C assures deeper trap depth ($E>kT$). However, optical fading is not a major disadvantage as it might be evaded by simply storing material in a light tight envelop M. Oberhofer *et al.* (1981).

### 2.4.10 Minimum Detectable Dose

The minimum detectable dose, lower detection limit or threshold dose are the terms that are used to express single concept of lowest detection limit for a TL dosimeter. It may be defined as thrice the standard deviation of background measurement of unirradiated dosimeters after subtraction of the dark current reading Furetta (2003). It depends on the chemical composition, geometry and TL dosimeter mass as well as on characteristics of TLD reader S. W. S. McKeever *et al.* (1995); Pagonis *et al.* (2006). Pagonis *et al.* (2006) estimated the minimum detectable dose using the following equation;

$$MDD = 3\sigma_{BKG}CF \tag{2.12}$$

where $\sigma_{BKG}$ represents standard deviation of zero dose measurement and $CF$ represent calibration factor given by;

$$CF = \frac{D_C}{\frac{1}{N}\sum_{i=1}^{N}(M_i - M_{oi})} \tag{2.13}$$

where $D_C$ represents calibration dose, $N$ is number of TL dosimeters, $M_i$ is measurement of $i^{th}$ TL dosimeter, and $M_{oi}$ is background measurement of $i^{th}$ TL dosimeter.

### 2.4.11 Reproducibility

Reproducibility is another valuable dosimetric feature that any TL dosimeter should demonstrate as consistency of readings over the repeated cycles is highly desirable for an economically suitable TL dosimeter. Reproducibility is termed as stable physical properties of TL material that consequently leads to reproduceable dosimetric characteristics. Most of TLD materials are re-useable over many cycles without noticeably altering the dosimetric characteristics if irradiated within saturation dose limit. Consequently, dosimeter reproducibility can be estimated to a given dose level by determining standard deviation of repeated measurements for single dosimeter under similar conditions, because of adequate knowledge about dosimeter stability M. Oberhofer *et al.* (1981).

## 2.5 Magnesium Borate based TL Dosimeter

The Magnesium Borate based TL dosimeters are of interest, for radiation dosimetry especially in radiotherapy and clinical radiation dosimetry, due to their low $Z_{eff}$, cheaper cost and simple handling, thus, it has been explored intensively by many researchers since 1974. However, extensive research has been conducted, through these years, to explore the dosimetric features of rare earth doped Magnesium Borates. Whereas, the role of transition metals as activators, has also been explored by different researchers. Besides, the effects of Alkali metals, as co-activator, on dosimetric characteristics of rare earth or transition metal activated Magnesium Borates has also been explored.

The first attempt to explore the possible application of rare earth doped Magnesium Borate in radiation dosimetry was made by Kazanskaya and his team in 1974. They reported the dosimetric properties of polycrystalline Magnesium Borate activated with Dysprosium. The material demonstrates a well-defined dosimetric peak between 190 $^oC$ and 200 $^oC$. The material was reported to be 10 to 20 times more sensitive as compared to standard TLD-100. The energy response at 40 keV is about 30% higher as compared to standard TLD-100. The dose response is observed to be linear from $10^{-5}$ to 10 Gy. The material demonstrated 25% fading over 40 days when stored at room temperature Kazanskaya *et al.* (1974).

In another study M. Prokić (1980) reported Dy and Tm activated Magnesium Borate. The newly developed TL material is reported to be 7 times more sensitive as compared to standard TLD-100 with an increased linear dose range from $10^{-5}$ to 102 Gy. Further studies by Barbina and Driscoll identified batch variability which suggested the necessity of an improved preparation method to avoid individual detector calibration which is quite laborious process when preparing the dosimeters for dose monitoring on wide range in personal and environmental dosimetry Barbina *et al.* (1981); Driscoll *et al.* (1981).

However, Furetta and his team made a successful attempt to overcome the reproducibility issue by activating $MgB_4O_7$ with Dy + Na. A single dosimetric peak is observed at 190 $^oC$. The results show that the introduction of Na as a second dopant enhance the thermoluminescence intensity without shifting the dosimetric peak temperature. The significance of the match between spectral emission of the TL material and the sensitivity of PMT of TLD reader to the emitted light is demonstrated by comparing the TL sensitivity of the same TL material measured with different TLD reader that shows that the relative TL sensitivity is dependent on the spectral response of the TLD reader. The relative sensitivity is reported to be 6-15 as compared to standard TLD-100 depending upon the TLD reader type. The reported reproducibility is within 2% from 1 mGy to 0.25 Gy with an effective linear dose range from $6\times10^{-8}$