Eu/Mg-DOPED SODIUM SILICA-BORATE GLASSES FROM RECYCLED SODA-LIME-SILICA GLASS FOR LOW-DOSE RADIATION DOSIMETRY

NABASU SETH EZRA

UNIVERSITI SAINS MALAYSIA

2025

Eu/Mg-DOPED SODIUM SILICA-BORATE GLASSES FROM RECYCLED SODA-LIME-SILICA GLASS FOR LOW-DOSE RADIATION DOSIMETRY

by

NABASU SETH EZRA

Thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

July 2025

ACKNOWLEDGEMENT

The tale of several prosperous years without any remnants of calamities is evidence of God's dwelling in each phase of my life. Firstly, I would like to express my profound gratitude to my friendly and engaging supervisor, Assoc. Prof. Dr. Iskandar Shahrim Mustafa for the supervisory role played in this research work, as well as for his scientific and moral support, guidance, and encouragement throughout this research journey. Your brilliance will always be an inspiration to me. In addition, I want to heartily acknowledge Dr. M.I. Sayyed, a friend and mentor from Jordan, for his support, encouragement and for ensuring that this research becomes a useful facility in the field of knowledge.

Furthermore, this work could not have existed without the inspiration, support, and love of my lovely wife, Mrs Nabasu Blessing Seth, my mother, Mrs Nabasu Na'omi, and my siblings. I pause to sincerely appreciate and thank all my friends in Nigeria and Malaysia, most especially my friend-turned-brother, Alvin Cheong and his lovely wife, Juneta Balacuit, a family I met in Penang English Seventh Day Adventist Church (PESDAC), Malaysia. I was at home in Malaysia because of the love I received from the PESDAC family. May GOD reward you all.

Lastly, to all my well-wishers from within and without, I say thank you a bunch. Remember, "the memories of goodhearted individuals endure even when the ocean of remembrance runs dry …"

Nabasu Seth Ezra

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

α_e	Electronic polarization
α_m	Molar polarizability
R_L	Reflection loss
R_m	Molar Refractive Index
ε_{opt}	Optical Dielectric Constant
A_w	Atomic weight
F_w	Fractional weight
M_{wt}	Molecular weight
V_m	Molar volume
Z_{eff}	Effective atomic number
r_i	inter-nuclear distance
r_p	Polaron radius
α_{me}	Molar electronic polarizability
δ_d	Dislocation density
σ_A	Standard Deviation
F	Field strength and Calibration factor
M	Metallisation criterion
n	Refractive Index
N	Ion concentration
T	Optical Transmission
Xc	Diffraction angle
ε	Dielectric Constant
D	Crystallite size
ρ	Density

LIST OF ABBREVIATIONS

B_2O_3	Boron Trioxide
BO	Bridging Oxygen
CaO	Calcium Oxide
CV	Covariance
DVI	Detector Variability Index
EDX	Energy Dispersive X-ray
Eu_2O_3	Europium Oxide
FE-SEM	Field Emission Scanning Electron Microscopy
FS	Field Size
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
LDL	Low Detectable Limit
MDD	Minimum detectable dose
MFP	Mean Free Path
$MgSO_4$	Magnesium Sulphate
Na_2O	Sodium Oxide
NaSBEu	Sodium Silica Borate Europium
NaSBEuMg	Sodium Silica Borate Europium Magnesium
NBO	Non-Bridging Oxygen
OPD	Oxygen Packing Density
OSL	Optically Stimulated Luminescence
PL	Photoluminescence
RE	Rare-Earth
REO	Rare-Earth Oxide
RPL	Radio-Photoluminescence

RVI	Reader Variability Index
RWG	Recycled Window Glass
SE	Secondary Electron
SiO_2	Silicon Oxide
SLS	Soda Lime Silica
SSD	Source to Surface Distance
STD	Standard Deviation
SVI	System Variability Index
TL	Thermoluminescence
TLD	Thermoluminescence Dosimeter
TSL	Thermally Stimulated Luminescence
TTP	Time-Temperature Profile
UV	Ultraviolet
XRD	X-ray Diffractometer
XRF	X-ray Fluorescence
Z_{eff}	Effective atomic number

KACA NATRIUM SILIKA-BORAT TERDOP Eu/Mg DARIPADA KACA SILIKA SODA-KAPUR KITAR SEMULA UNTUK DOSIMETRI RADIASI DOS RENDAH

ABSTRAK

Kajian ini mensintesis dosimeter sinaran dengan kaca soda-limau-silika (SLS), yang biasanya dibuang di tapak pelupusan sampah, di mana ia mengambil masa yang lama untuk rosak. Menggunakan sisa kaca ini membantu mengelakkan pengumpulan sisa kaca. Di samping itu, ini mengurangkan keperluan untuk SiO_2 tulen. Dua set gelas telah disintesis dengan pelindapkejutan cair, kaedah konvensional, didop dan didop bersama dengan Eu_2O_3 dan $MgSO_4$ masing-masing dengan komposisi $(Eu_2O_3)_x$ $(Na_2O)_{0.1}$ $(B_2O_3)_{0.6}$ $(SLS)_{0.3-x}$ dan $(Eu_2O_3)_{0.01}$ $(Na_2O)_{0.1}$ $(B_2O_3)_{0.6}$ $(SLS)_{0.29-y}$ $(MgSO_4)_y$ di mana x = y = 0, 0.005, 0.01, 0.03, dan 0.05 mol%. Analisis XRF digunakan untuk solek kimia sampel kaca SLS. Alat ketumpatan digunakan untuk pengukuran ketumpatan, XRD mengesahkan kehabluran separa sampel, FE-SEM digunakan untuk morfologi permukaan, EDX untuk analisis unsur, IR dan Raman digunakan untuk ikatan struktur, dan spektrofotometer UV digunakan untuk sifat optik. Sejumlah 70.81% berat SiO_2 ditemui daripada analisis XRF. Berat molekul yang lebih besar dan jejari atom Eu_2O_3 dan $MgSO_4$ menaikkan ketumpatan daripada 2.220 kepada 2.620 dan 2.214 kepada 2.285 g/cm^3, dan kehadiran Na_2O menghasilkan lebih banyak NBO, dengan itu meningkatkan isipadu molar daripada 29.764 kepada 30.3753. cm^3/mol, masing-masing dengan itu mengembangkan kaca. Peningkatan dalam ion Eu^{3+} menurunkan $\boldsymbol{r_p}$ dan $\boldsymbol{r_i}$, dengan itu menaikkan F daripada 3.718 kepada 16.914, manakala peningkatan dalam ion Mg^{2+} menurunkan $\boldsymbol{r_p}$ dan $\boldsymbol{r_i}$ dan juga menaikkan F

daripada 3.654 kepada 16.653. Semua spektrum inframerah (FTIR) sampel kaca memaparkan banyak puncak penyerapan, dan puncak penyerapan ini terhasil daripada kelonggaran ikatan trigonal BO_3, yang menyebabkan regangan getaran asimetrik borat. Eu^{3+} dan Mg^{2+} meningkatkan penyerapan optik kaca, meningkatkan kebolehpolaran, dan menunjukkan sifat tak linear yang menjanjikan. Sampel yang disintesis telah didedahkan kepada sinar-X dengan potensi tiub 80 kVp, jarak permukaan sumber (SSD) 100 cm, beban tiub 64 mAs dan saiz medan 5x5 cm^2 dan pembaca Harshaw 3500 TLD digunakan untuk bacaan. Doping bersama $MgSO_4$ meningkatkan tindak balas TL NaSBEu0.01 conc. (optimum bagi gelas NaSBEu), manakala NaSBEuMg0.03 conc. adalah optimum set cermin mata NaSBEuMg. Untuk sifat TL kaca NaSBEuMg0.03, tindak balas dos adalah linear sehingga 300 mGy, dan selepas 90 hari, kehilangan isyarat kira-kira 50% telah disahkan daripada penemuan. MDD didapati sekitar 0.74 mGy, manakala sensitiviti adalah 13.265 nC mGy^{-1} g^{-1} (cerun lengkung tindak balas dos). Untuk kebolehulangan, indeks kebolehubahan pengesan (DVI) ialah 0.130%, dan nombor atom berkesan, $\boldsymbol{Z_{eff}}$ ialah 9.6, setanding dengan tulang. Keputusan ini menyerlahkan potensi gelas NaSBEuMg0.03 untuk dosimetri sinaran dos rendah sambil memajukan kemampanan melalui kitar semula kaca SLS yang inovatif.

Eu/Mg-DOPED SODIUM SILICA-BORATE GLASSES FROM RECYCLED SODA-LIME-SILICA GLASS FOR LOW-DOSE RADIATION DOSIMETRY

ABSTRACT

This study synthesised a radiation dosimeter with soda-lime-silica (SLS) glass, which is typically thrown in landfills, where it takes a long time to break down. Using this glass waste helped prevent the build-up of glass waste. Additionally, this reduces the need for pure SiO_2. Two sets of glasses were synthesised by melt-quenching, the conventional method, doped and co-doped with Eu_2O_3 and $MgSO_4$ respectively with compositions $(Eu_2O_3)_x$ $(Na_2O)_{0.1}$ $(B_2O_3)_{0.6}$ $(SLS)_{0.3-x}$ and $(Eu_2O_3)_{0.01}$ $(Na_2O)_{0.1}$ $(B_2O_3)_{0.6}$ $(SLS)_{0.29-y}$ $(MgSO_4)_y$ where x = y = 0, 0.005, 0.01, 0.03, and 0.05 mol%. An XRF analysis was used for the SLS glass sample's chemical makeup. A density apparatus was used for the density measurement, XRD confirms the partial crystallinity of the samples, FE-SEM was used for the surface morphology, EDX for elemental analysis, IR and Raman were adopted for the structural bonding, and a UV spectrophotometer was utilised for the optical properties. An amount of 70.81 wt% of SiO_2 was discovered from XRF analysis. The larger molecular weight and atomic radius of Eu_2O_3 and $MgSO_4$ raised the density from 2.220 to 2.620 and 2.214 to 2.285 g/cm^3, and the presence of Na_2O results in creating more NBOs, hence raising the molar volume from 29.764 to 30.753 and 31.130 to 31.479 cm^3/mol, respectively thereby expanding the glass. The increase in Eu^{3+} ions decreased the r_p and r_i, thereby raising the F from 3.718 to 16.914, while an increase in Mg^{2+} ions decreased the r_p and r_i and also raised F from 3.654 to 16.653. All glass samples' infrared spectra (FTIR) displayed many absorption peaks, and these absorption peaks result from the

trigonal BO_3 bond's relaxation, which causes asymmetric vibrational stretching of the borate. Eu^{3+} and Mg^{2+} improved the glass's optical absorption, increased polarizability, and showed promising nonlinear properties. The synthesised samples were exposed to X-rays with 80 kVp tube potential, a source-surface distance (SSD) of 100 cm, tube load of 64 mAs and a field size of 5x5 cm^2 and a Harshaw 3500 TLD reader was used for the readout. $MgSO_4$ co-doping enhanced the TL response of NaSBEu0.01 conc. (the optimum of NaSBEu glasses), whereas NaSBEuMg0.03 conc. was the optimum of the NaSBEuMg set of glasses. For the TL properties of NaSBEuMg0.03 glass, the dose response was linear up to 300 mGy, and after 90 days, an approximately 50% signal loss was verified from the findings. The MDD was found to be around 0.74 mGy, while the sensitivity was 13.265 nC mGy^{-1} g^{-1} (slope of the dose-response curve). For the reproducibility, the detector variability index (DVI) was 0.130%, and the effective atomic number, Z_{eff} was 9.6, comparable to that of bone. These results highlight the potential of NaSBEuMg0.03 glasses for low-dose radiation dosimetry while advancing sustainability through the innovative recycling of SLS glass.

CHAPTER 1

INTRODUCTION

1.1 Background

Applications of radiation and nuclear technologies in industry, science, and medicine are intrinsically connected to measurements of the energy received by the substance. The radiation dose absorbed by a substance determines the effects radiation has on that substance. Due to this fact, the development of dosimetric techniques and the use of procedures involving ionising radiation have always been intertwined. Currently, several dosimetric systems are commercially available, with thermoluminescence dosimeter (TLD) systems (based on Al_2O_3 or LiF detectors) being the most popular ones, and they are the most widely used dosimetric technique worldwide. The phenomenon of thermoluminescence was first noticed by Boyle in 1633 when he noticed shimmering light coming from a warmed diamond in the dark (Gasiorowski & Szajerski, 2019). Abdel-Razek (2016); and Attix (2008) defined thermoluminescence (TL) as the process of a semiconductor or an insulator emitting light because of heating up after having previously absorbed energy from radiation. Jena et al. (2023) defined it as the process by which some crystalline substances, when heated, absorb radiation-carried energy and then release it as light (visible electromagnetic radiation)

A "TL glow curve" is a graph that relates the temperature of the sample to the amount of light produced during the TL procedure. For efficient TL dosimetry, the essential features include a simple glow curve, stability, increased dose sensitivity, dose linearity, commercial availability, simplicity of production, dependability, and reduced production costs (Nair et al., 2022). Thermoluminescence has been a hub of intense research in recent years because of its numerous applications. Radiation dosimetry has been TL's most notable application to date. Because of their long-term storage capabilities, dose independence from radiation intensities, simplicity of measurement, and light packaging, numerous dosimetric problems have been resolved with the help of ionising radiation dosimeters, which rely on the TL characteristics of materials.

The term "radiation dosimeter" refers to a tool, equipment or system that, either directly or indirectly, detects or evaluates radiation exposure levels like the absorbed dose or equivalent dose (KERMA). Directional dependency, linearity, energy response, dose rate or dosage reliance, accuracy and precision, and spatial resolution are preferable dosimeter properties. Not all requirements can be satisfied by every dosimeter. As a result, it is possible to choose the radiation dosimetry system by carefully considering the radiation environment (Hanne et al., 2005; Yan & Moros, 2006).

The search for more radiation-detection products (radiation dosimeters) is extremely important from a technological standpoint. This is especially true for the medical and food industries, where there is a constant requirement for in-situ measurements that are made impossible by the conventional sensors' fragility and bulk (Kowatari et al., 2016; De Oliveira et al., 2018; Fedorov & Viskanta, 2000; O'Keeffe et al., 2008). It is crucial to monitor the radiation dose in diagnostic radiology to minimise excessive exposure. The popularity of interventional radiology (IVR) techniques has been increasing annually due to their invasive nature compared to surgical procedures (Clement et al., 2012). Radiation skin damage has been described in IVR methods (Valentin, 2000); therefore, measuring the entrance skin dose (ESD) is essential for interventional radiology. Various dosimeters have been used to evaluate ESDs for diagnostic kilovoltage X-ray beams (Ma et al., 2001; Hill et al., 2014).

TLDs are comprehensive dosimeters, but they have significant energy dependence when used with low-energy X-ray beams. Although meeting all these requirements can be difficult, the ideal dosimeter for measuring ESD should be small, highly sensitive, and have properties of tissue or water equivalency as well as real-time dosimetry (Zarzycki, 1982; Mohd Zaid et al., 2016). Phosphors for thermoluminescence dosimetry (TLD) are alkaline-earth sulphates doped with rare-earth ions. Combined with rare earth oxides (Eu_2O_3), magnesium sulphate ($MgSO_4$) has been utilised to create potent phosphors for thermoluminescence dosimetry (Naeem, Mustafa, Yusof, Thabit, et al., 2024).

It is commonly known that in the global glass-making industry, soda-lime-silica (SLS) has the highest production volume (Shelby, 2020; Varshneya, 2013). Its applications include consumer goods like cooking utensils, window glass, and glass containers, as well as more contemporary, high-tech products like photovoltaic solar panels and microfluidic gadgets (Shelby, 2020; Mattos, 2012; Lin et al., 2001; Flocker & Dharani, 1997; Mauro, 2014). Although SLS glass is appealing due to its optical qualities, durability, recycling potential, and affordability, the presence of alkali ions in the glass increases its external reactivity in humid environments. This can lead to surface hydration, corrosion, and degradation of mechanical intensity and optical response (Surdyka et al., 2014). Due to its easy colour change reaction to radiation, its capacity to replicate bone absorption, its affordability, and its widespread availability, soda-lime-silica glass is a useful instrument in radiation dosimetry (Freiman et al., 2009).

Recycling raw materials is essential to any modern society, and its benefits cannot be overstated. Recycling is beneficial in modern society because it conserves natural resources and lessens the quantity of waste that ends up in landfills and incinerators like timber, water, and minerals, reduces the need to gather new raw materials, which strengthens the economy's security, conserves energy, and creates job opportunities in the recycling and production industries (Mohd Zaid et al., 2016; Chinnam et al., 2013).

1.2 Problem Statement

The effects of radiation on a substance depend on the amount of radiation that the substance absorbs. As a result, utilisation of ionising radiation processes and the development of dosimetric techniques have always been linked. Many dosimetric systems are currently available, including thermoluminescence dosimeters (TLD).

Researchers have investigated the dosimetric properties of glass, and their findings indicate that glass is an effective dosimetric material (R. S. Omar et al., 2019)(Mhareb, Alajerami, et al., 2020). However, SLS (SiO_2) glass is a non-phosphor material (materials that do not emit visible light upon interaction with electrons), therefore its presence in the glass network will reduce its effectiveness for low-dose radiation dosimetry or its presence in the composition will not make a good TL dosimeter because there will be less or no trapping of electrons in the band gap, which will correspond with the release of less or no visible light (bad glow curve).

Hence, this thesis wishes to assist in making this non-phosphor material a phosphor through doping with Eu_2O_3, a rare-earth metal oxide, which will serve as an impurity to aid in trapping the electrons after exposure to X-rays. The co-dopant $MgSO_4$ will further enhance the sensitivity of the Eu_2O_3-doped set of glasses, thereby making the Eu_2O_3-doped $MgSO_4$ co-doped sodium silica-borate glasses a sensitive low-dose TL dosimeter with good dosimetric characteristics.

Furthermore, soda lime silica (SLS) glass is a non-biodegradable material which decomposes slowly. As a result, glass waste builds up. To address this environmental concern, researchers are investigating the possibility of recycling SLS glass waste as an alternative SiO_2 source (Djouider, 2020; Thumsa-Ard et al., 2017). Recycling SLS glass as a SiO_2 source minimises the costs of production of pure SiO_2, reduces the amount of waste disposed into landfills and incinerators, saves natural resources, and lessens the necessity to gather fresh raw materials, thereby enhancing the security of the economy and preserves energy.

This thesis will offer a means for disposing of soda lime glass to save natural resources, prevent trash from building up, and utilise this waste soda lime glass alongside other materials to make a TL dosimeter for low-dose radiation dosimetry by doping and co-doping with Eu_2O_3 and $MgSO_4$, respectively.

1.3 Research Objectives

i) To synthesise Eu_2O_3-doped and $MgSO_4$-co-doped Na_2O silica-borate glass samples from recycled SLS glass by melt quenching.

ii) To physically, optically and structurally characterise the Eu_2O_3-doped and $MgSO_4$-co-doped Na_2O silica-borate glass samples.

iii) To optimise the TL response of the synthesised Eu_2O_3-doped and $MgSO_4$-co-doped Na_2O silica-borate glass samples.

iv) To determine the dosimetric characteristics of the optimum $MgSO_4$-co-doped Eu_2O_3-doped Na_2O silica-borate (NaSBEuMg) glass TL dosimeter.

1.4 Scope of Study

The researcher chose to fabricate the glasses by melt-quenching, the conventional method. After taking note of the melting points of each element in the composition, the researcher used a maximum temperature of 1200 °C at 10 °C/min and held for 2.5 h for the complete melting of the constituent.

The research focused on the fabrication process, characterisation, and dosimetric evaluation of the glass samples. There are many commercial glass wastes in the world, such as recycled window glass, transparent walls, windscreens, kitchenware, watch glass, fibre optic, etc., but this research work focuses on a common colourless waste bottle which is used globally.

To measure the structural characteristics of the glass network, XRF, XRD, FE-SEM, EDX, FTIR, and Raman techniques were adopted at room temperature. For the physical characteristics, the samples' density was determined utilising the Archimedes principle. A UV-1800 SHIMADZU UV spectrophotometer operating at room temperature was used to measure the samples' optical properties with a 200 to 800 nm wavelength range. Furthermore, the samples were exposed to X-rays using the conventional X-ray machine and then heated with a Harshaw 3500 model TLD reader to determine the glow curve.

1.5 Significance of the Study

The discovery of additional products that can detect radiation is hugely important in terms of technology. This is principally true in the medical and food industries, where there is a high demand for in-situ measurement, which is frequently not possible because of the frailty and small size of standard sensors. It is crucial to understand the radiation dose received during X-ray examinations to minimise excessive exposure. Glass has been used for dosimetry since 1953, and research on its dosimetric properties continues today.

The management of waste glasses will help in decreasing the environmental and health hazards linked with discarding them and the shortage of the area of land necessary for disposing of them. Consequently, the primary idea of this work is to find a way of recycling SLS glasses, which form the largest amount of waste-like glass to make radiation dosimeters, since SLS glass can easily be obtained due to its availability globally and is inexpensive. It can help in reducing the dependence on raw materials to produce radiation-measuring devices, and one advantage of using glass for radiation detection is that it can be manufactured in compact sizes.

Glasses doped with RE illustrate a powerful class of photonic materials because of numerous essential preferences over their sparkling counterparts. When used appropriately, rare-earth (RE) elements and alkaline-earth metals can significantly improve glass's mechanical, chemical, and thermal stability.

1.6 Thesis Design

In chapter 1, the readers are introduced to the primary concerns of the work, outlining its introduction, problem statement, research objectives, scope of study, and significance. Chapter 2 presents an observational and theoretical structure for the present study, drawing from the most recent literature. Details on the interaction of radiation with matter are given here. The chapter also tries to explain what SLS glass is all about and how researchers have used it. It also deals with radiation dosimeters, paying exceptional attention to TL dosimeters, their properties and exigencies depending on the application field. An overview of the elements included in the composition is also given in this chapter. The tools and techniques utilised to carry out the study's suggested goals are detailed in Chapter 3. Chapter 4 contains the research results and a discussion of the findings, while Chapter 5 concludes with suggested next directions.

CHAPTER 2

LITERATURE REVIEW

2.1 Silica-Rich Waste

Silica (silicon dioxide) is one of the most vital raw minerals present on earth, and silica in optoelectronic applications is most often white. Silica can occur in the states of gel, crystalline, and amorphous. It is frequently utilised as a precursor for a range of items in synthetic chemistry applications, including thin films, coatings, and catalysts for electronic and optical materials. Other applications for it include ceramics, chromatography, anticorrosion agents, and catalysts. Because of its excessively high melting point of 1700 °C, the utilisation of high-purity silica in commercial applications is extremely expensive. Thus, one method being used by researchers today to reduce the cost of employing high-purity silica is the derivation of silicon dioxide from agricultural waste and also from soda-lime silica (SLS) glass. Much research has been done on using silica from agricultural waste, including rice husk (Ruengsri et al., 2015), palm waste (Faizul et al., 2014), maize cob ash (Velmurugan et al., 2015), coconut husk (Anuar et al., 2018), and sugarcane bagasse (Norsuraya et al., 2016). Silica can also be obtained through recycling soda lime silica glass, because a high percentage of silica has been recorded in literature from recycled soda lime glass (Ezra et al., 2024)(Hisham et al., 2021).

Furthermore, to lower the cost of chemical supplies and waste disposal, researchers are interested in utilising recycled SLS glass as an alternative silicon dioxide source. This is because SiO_2, Na_2O, CaO, Al_2O_3 and other oxide components make up SLS glasses, with SiO_2 making up as much as 73.0 wt.% of the total (Zaid et al., 2012). The particular qualities of silica, such as its high service temperature, resilience to thermal shock, chemical durability, and low electrical conductivity, make silica glass useful in a variety of applications by adding other oxides such as alkaline-earth sulphates doped with rare-earth ions ($MgSO_4$ and Eu_2O_3) to modify the properties for radiation dosimetry (Kumar et al., 2023). Wahib et al. (2019) compared the effectiveness of each glass for radiation measurement by looking at the TL dosimetric characteristics of five glass-based commercial cookware brands originating from differing nations: Godis-China, Reko-China, Glass Tum-Malaysia, Skoja-France, and Lodrat-France. A study of the conduct of zinc-oxide-doped recycled window glass (RWG) as a TL dosimeter was carried out by Thumsa-Ard et al. (2017). (Laopaiboon & Bootjomchai, 2015a) worked on the TL and physical characteristics of recycled window glasses (RWG) arranged for the measurements of radiation dosimetry. Moffatt et al. (2012) studied the luminescence characteristics of common glasses for use in retrospective dosimetry. They examined the TL characteristics of 17 samples of household and laboratory glasses applicable to retrospective population dosimetry.

2.1.1 Recycled SLS Glass

Manufacturing industries are central to every country's economic advancement. However, it generates enormous amounts of waste, such as glass waste, which calls for a different way of thinking to handle solid waste. Thus, there is a new idea in the country to make these solid wastes more useful, advantageous to society, and environmentally benign (Mohd Zaid et al., 2016). Among silica-loaded wastes, soda lime glass is currently being used as a silica source to create inexpensive glass because of the potential for reduced energy costs due to the low melting temperature at 1400 °C (Khaidir et al., 2019a). The most prevalent type of glass is soda-lime glass, employed for window panels, glass bottles (beverages, food jars and bottles, and some basic goods), container products, and insulating materials that have received much attention (Bateni et al., 2014).

SLS is a widely used industrial glass material that accounts for 90-95% of global glass production. (Matori et al., 2010). Its relatively low melting point, resilience to chemicals, electricity, and mechanical forces, ability to transmit visible light, and inexpensive production make it suitable for usage in a wide range of industries (Kurtulus et al., 2021). Soda-lime glass is comprised of SiO_2, Na_2O, CaO, MgO, Al_2O_3, plus minor compounds. According to Shelby (2020), the compounds that comprise windows manufactured by commercial SLS glass models include SiO_2-73%, Na_2O-14%, CaO-9%, MgO-4%, and others and SiO_2-74%, Na_2O-13%, CaO-11%, MgO-0.2%, and other materials make up the containers. Because SLS glasses form good glass and have favorable chemical hardness, elevated transparency, low melting point, elevated thermal stability, and beneficial RE ion solubility, they are considered an appealing host matrix for RE ions. Soda-lime glasses are primarily composed of SiO_2, Na_2O, and CaO (Omar, Fen, Matori, Zaid, et al., 2016a; Chimalawong et al., 2012; Kaewwiset et al., 2012). According to Çetin et al. (2017), SLS glass proves to be a desirable material due to its optical transparency, unusual resistance to chemicals, sensible and acceptable mechanical properties, and insulating qualities.

Different approaches have been used by researchers to evaluate the components of SLS glass. X-ray Fluorescence (XRF) spectroscopy was utilised by (Khazaalah, Mustafa, Al-Ghamdi, et al., 2022) to identify the oxide compounds contained in the SLS glass sample. They found that the following elements were present: 74.1% SiO_2, 12.91% Na_2O, 9.69% CaO, 0.4% MgO, 1.54% Al_2O_3, 0.59% K_2O, 0.02% P_2O_5, 0.11% Fe_2O_3, 0.04% TiO_2, and 0.01% MnO. (Bootjomchai & Laopaiboon, 2014) determined 73.3900% SiO_2, 15.1700% Na_2O, 7.3390% CaO, 3.4030% MgO, 0.5866% Al_2O_3, 0.0635% Fe_2O_3, 0.0263% TiO_2, 0.0238% K_2O using Wavelength Dispersive X-ray Fluorescence (WDXRF) study. To assess the percentage of oxide components in the SLS glass, Energy Dispersive Spectroscopy (EDS) was utilized (Djouider, 2020), and the results showed that there were 23.30% SiO_2, 9.11% Na_2O, 5.07% $CaCO_3$, 56.82% O, 2.35% MgO, 0.45% Al_2O_3, 0.48% K_2O, 2.42% CaO. Ahmad et al. (2018) employed XRF to investigate the SLS glass's constituent parts. They found that a range of materials, including 2.2% Al_2O_3, 13.7% Na_2O, 9.93% CaO, 1.64% MgO, and 68.54% SiO_2, are present in the SLS glass.

2.2 The Glass as a Thermoluminescent Material

Glass has been applied for dosimetry since 1953 (Schulman et al., 1953). Work on glass dosimeters is still ongoing. Several glass brands have been used in badge dosimetry methods. All these processes rely on the principle of TL, which is the discharge of light when a semiconducting material is heated after being irradiated. Normally, the measure of emitted light corresponds to the dose absorbed in the dosimetric medium. (Knoll, 2000). The mechanism of the phenomenon of TL is presented in Figure 2.1.

Nowadays, numerous dosimetric systems are available on the market, with the most common being alanine-based EPR dosimetric systems and TL systems, which use Al_2O_3 or LiF-based TLD detectors. The most frequently employed dosimetric technique globally is TL dosimetry. Skwarzec (2011) told of the luminescence of fluorite and other materials when heated after being exposed to radium radiation.

TL dosimeters, mainly used for environmental and personal dose monitoring, typically rely on LiF and are currently the most popular choice. Lithium fluoride is preferred due to its beneficial properties, including a high sensitivity, a low minimal dose, and minimal loss of signal over time, as well as a quick method for readout (Piaskowska et al., 2013). Many artificial and natural materials have been approved in TL studies. Natural materials are Al_2O_3, BeO_2, and CaF_2 (fluorite); artificial materials include LiF:Mg,Ti; LiF:Dy; LiF:Mg,P,Cu; $Li_2B_4O_7$:Mn; $CaSO_4$:Dy; and $Li_2B_4O_7$:Cu. In dosimetry, LiF:Mg,Ti represents the most commonly employed material, and is commercially known as TLD-100 (Nair et al., 2022).

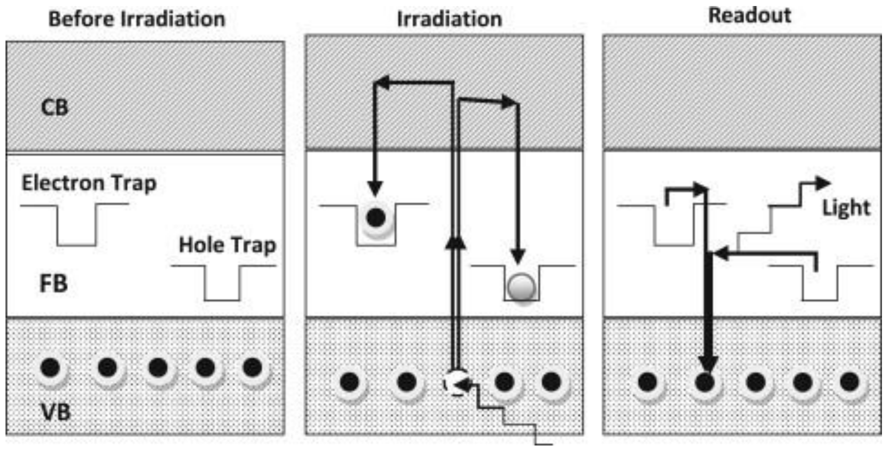

Figure 2.1 The phenomenon of thermoluminescence (Rivera, 2012).

2.2.1 TLD Properties

2.2.1(a) Glow Curve

The correlation between luminescence intensity (I) and temperature (T) is illustrated by the glow curve. It can exhibit multiple TL peaks, signifying various trapping phases associated with different activators. Some of these peaks may be identifiable within the glow curve, while others may not be discernible. The glow peaks in the emission spectrum are formed due to the spectral distribution of energy emitted as TL light. The measurement of the dose absorbed in the phosphor can be expressed as either the peak height or the area under the glow curve. When utilizing peak height to gauge exposure or absorbed dose, it's crucial to ensure the heating cycle is highly reproducible to prevent variations in peak height (Furetta, 2003a). Therefore, it is possible to assert that any substance's TL properties can be characterized through its TL glow curve, with the heating rate specified. Consequently, the glow curve functions as the documentation of the TLD reading. The glow curve's nature is affected by a variety of controllable and uncontrollable factors, including the type and quantity of activator present in the TL material, the radiation type, the absorbed dose level, the rate of heating utilized during the sample's readout, prior thermal treatments such as cooling rate, non-radiation induced signals originating from both the TL reader and TL material, and the cumulative absorbed dose. Figure 1.1 presents the glow curve shape of TLD-100 (suitable for health and medical physics dosimetry applications) irradiated to 21 MeV electrons. In some materials, as the heating rate rises, the temperature of the glow peak shifts to higher values, and the intensity of the glow peak drops because of thermal quenching. As a result, it becomes necessary to fine-tune the heating rate for any newly invented dosimeter. Thus, when presenting a glow curve, it's important to specify the heating rate. With increased heating rates, there's a potential for glow peaks to merge because of thermal lag. In routine dosimetry measurements, the recording of the glow curve offers significant advantages since it has the ability to help detect equipment issues, such as inappropriate heating source–dosimeter thermal coupling, or unusual appearances of signals not caused by radiation (Basun et al., 2003; Mhareb et al., 2018).

It is possible for a glow curve to comprise of many peaks, each corresponding to a distinct trapping level in the material. This is because every trapping level in the material produces a corresponding glow peak. The glow curve may or may not resolve these peaks. The TL intensity has a direct relationship with the rate at which traps are emptied (Eqn. 2.1) (Furetta, 2003b).

$$I = -c\frac{dn}{dt} \tag{2.1}$$

Integrating Eqn. (2.1) provides the relationship between the thermoluminescence intensity and the potential number of glow peaks, expressed as Eqn. (2.2).

$$n(t) - n_{\infty} = \int_{t}^{\infty} I.dt' \tag{2.2}$$

When the glow curve has a single peak, Eqn. (2.2) will be written in a different format as Eqn. (2.3).

$$n(t) = \int_{t}^{\infty} I.dt' \tag{2.3}$$

where $n_{\infty} = 0$

2.2.1(b) Dosimeter Sensitivity

One of the TLD material's most important dosimetric characteristics is sensitivity. A common way to express a TLD material's sensitivity is via the TL response, in reader units, per unit of dose and unit of sample mass (Alajerami et al., 2014). The sensitivity can be expressed as Eqn. (2.4).

$$Sensitivity = \frac{TL\ intensity}{incident\ dose\ \times\ mass\ of\ TLD} \tag{2.4}$$

Numerous factors affect precise sensitivity, such as the kind and concentration of dopant utilised, while the TL measurements can be influenced by the TL reader employed, the optical filters, the heating rate, the sample's optical density, and any contamination on the surface of the sample. McKeever et al. (1995) proposed the concept of relative sensitivity in response to the limitations surrounding precise measurements of sensitivity. Eqn. (2.5) gives the comparison of the target materials' and the TLD-100's TL signals.

$$S(D)_r = \frac{S(D)_{TLD\,material}}{S(D)_{LiF:Ti,Mg}} \tag{2.5}$$

2.2.1(c) Time Temperature Profile (TTP)

From the TL dosimeter, the dosimetric data is extracted using a user-defined configuration. Several parameters, including the heating rate used during readout, the pre-heat temperature, and the maximum temperature at which the dosimetric information must be collected, are all controlled by the time temperature profile (TTP), which regulates the TL material's thermal treatment. As a result, the selection of thermal treatment affects the acquisition time. The TL material's glow curve is impacted by variations in the TTP, which are contingent upon the material's chemical composition. Thus, before measuring the TL for a novel TL material, the glow curve setting should be optimised (Bakhsh et al., 2018). Figures 2.2 and 2.3 illustrate the TTP of TLD-100 and of dysprosium-doped calcium magnesium borate glass subjected to Co-60 gamma.

Dosimeter	TTP	
LiF: Mg, Ti TLD-100	**Preheat**	
	Temp (°C)	50
	Time (sec)	0
	Acquisition	
	Max Temp (°C)	300
	Time (sec)	13.33
	Rate (°C/sec)	25
	Anneal	
	Temp (°C)	0
	Time (sec)	0

Figure 2.2 Time-temperature profile (TTP) used for TLD-100 readout (Sadeghi et al., 2015)

Setting	
Preheat	
Temperature	50°C
Time	0 s
Acquire	
Temperature rate	5°C s^{-1}
Max temperature	300°C
Time	50 s

Figure 2.3 Time-temperature profile (TTP) setting for the dysprosium-doped calcium magnesium borate glass subjected to Co-60 gamma ray TLD-reader (Paper et al., 2019)

2.2.1(d) Lower Detection Limit

The lower detection limit, also referred to as the minimum detectable dose (MDD) or detection threshold, can be defined as the lowest evaluated value that determines the performance requirements for environmental and/or personnel dosimetry, and for which the dosimeter's readout value differs significantly (at the 95% confidence interval) from the readout value of a unirradiated dosimeter (Han, 2007); Leonardo et al., 2013).

Furetta (2010) defined the lower detection limit, D, as 3 times the zero-dose reading's standard deviation (STD). It is dependent upon the TL dosimeter mass, geometry, and chemical composition, in addition to the TLD reader's features McKeever et al. (1995). Eqn. (2.6) gives the lower detection limit (LDL) according to Djouider (2020).

$$LDL = 3\sigma_{BKG}F \tag{2.6}$$

where σ_{BKG} represents the STD of zero-dose measurement and F the calibration factor of the TLD reader.

2.2.1(e) Reproducibility

Another important dosimetric characteristic that any TL dosimeter should have is reproducibility. A TL dosimeter that is economically viable should be able to consistently produce readings throughout multiple cycles. Stable physical characteristics of TL material that subsequently result in repeatable dosimetric characteristics are referred to as reproducibility. If exposed to radiation within the saturation dose limit, the majority of TLD materials can be reused for numerous cycles without appreciably changing their dosimetric properties. Hence, through adequate dosimeter stability understanding, it is possible to estimate the dosimeter reproducibility to a specific dose level through the calculation of the repeated measurements' STD for a single dosimeter under similar conditions (Bakhsh et al., 2018). The coefficient of variation CV_i (%) for the response of the ith glass chip dosimeter is used to evaluate the reproducibility of multiple measurements of the same TLD (Djouider, 2020). Eqn. (2.7) below provides this coefficient, Moor et al. (2008)

and Standardisation state that the TLD measurement's coefficient of variation CV_i (%), should not be greater than 10%.

$$CV_i\ (\%) = \frac{SD}{M_i} \times 100 \quad (2.7)$$

Where M_i is the average of the reading values of the ith glass chip dosimeter and SD is the STD of these readings.

2.2.1(f) Fading

When thermal and optical stimulation release electrons and holes from their traps, they recombine, a statistical phenomenon known as fading. Because of intricate influencing components that in a natural setting are challenging to control, fading becomes an undesirable property of TL material, particularly in environmental radiation measurement. Lee et al., (2015) provided the fading phenomena likelihood as a temperature function (Eqn. 2.8).

$$P = S\ e^{\left(-\frac{E}{kT}\right)} \quad (2.8)$$

Where T is absolute temperature, k is Boltzmann's constant, S is frequency factor, E is activation energy, and P is transition probability. The equation illustrates how the frequency factor S, trap depth E, and absolute temperature T all affect fading behaviour. Eqn (2.9) provides the glow peak half-life, which is used to describe the time it takes for trapped electrons to reduce to half their initial population.

$$\tau = \frac{1}{P}(0.693) \quad (2.9)$$

Where P represents the transition probability.

The TL material at room temperature should ideally present no signal loss; nevertheless, if only slight fading occurs, the material's stability is considered to be good. Ensuring a maximum 200-250 °C peak temperature guarantees a deeper trap depth ($E > kT$). Fortunately, optical fading is not a significant drawback, as it is possible to avoid this through the material's storage in a light-tight enclosure, as suggested by (Lee et al., 2015).

2.2.1(g) Effective Atomic Number (Z_{eff})

For personal and medical radiation dosimetry, tissue equivalency represents the optimum dosimetric feature of a TL dosimetric material. For precise measurements, it is a desired dosimetric characteristic. Tissue-equivalent dosimetric materials are those whose effective atomic number (Z_{eff}) is comparable to that of human tissue (Z_{eff}= 7.4). In the context of radiological dosimetry, where there is a predominance of photoelectric interaction up to 100 keV, tissue equivalency is crucial. As a result, at photon energies less than 100 keV, TL dosimeters with high Z_{eff} are extremely sensitive (Furetta, 2003a). Each dosimeter material element has an elemental cross-section, denoted as α Z^x, where x varies between one and five depending on the type of interaction that occurs. The photon interaction cross-sections are in direct proportion to the atomic number, Z, raised to a certain numerical power. Reports indicate that its photoelectric effect value is 2.94 or 3.75. From the mass numbers, A_i, the atomic numbers, Z_i;, and the percentage mass composition of the element, *i*, to the sample f_i, the Z_{eff} can be calculated according to Eqn (2.10) (Jafari et al., 2014a).

$$Z_{eff} = \left[\sum \frac{f_i (Z/A)_i}{\sum f_j (Z/A)_j} * Z_i^a\right]^{\frac{1}{a}} \quad (2.10)$$

with a as an empirical number, which was taken to be 2.94.

2.2.1(h) Batch Homogeneity

A batch of TLDs is a collection of TLDs produced simultaneously under comparable synthesising conditions that have the same chemical composition, same irradiation, and same thermal background. On the other hand, homogeneity is a behavioural requirement that dictates TLDs should yield results that are essentially the same. Of significant concern is the homogeneity between newly synthesised TLD batches owing to its importance in large-scale dosimetric applications like personal radiation dose monitoring and environmental radiation monitoring, where calibration on an individual basis is not employed. Batch homogeneity remains a user-dependent TLD feature, despite the International Electrotechnical Committee establishing a standard tolerance limit for personal dosimetry in terms of the acceptance or rejection of the TL dosimeter. Depending on the application field, the user sets tolerance limits to determine the batch homogeneity. The utilization of dosimeters in contemporary radiotherapy techniques may pose a risk due to the substantial precision error in dose estimation caused by the extended tolerance limit, which amounts to 20-30% of the mean response. Clinical radiation dosimetry requires high precision in dose measurement; therefore, individual calibration factors based on calibration exposures can be used to correct the dosimeter response. The systemization method is also very important because it has a significant impact on batch homogeneity, even though it is a user-dependent property. Depending on the synthesis technique, for the determined tolerance limits, the batch homogeneity can differ significantly (Furetta, 2003; Bakhsh et al., 2018). Eqn. (2.11) expressed the uniformity test, which can be used to determine the batch homogeneity (Furetta, 2003).

$$\Delta_{max} = \frac{(M - M_O)_{max}(M - M_o)_{min}}{(M - M_o)_{min}} \times 100 \leq 30 \quad (2.11)$$

where M_O is the background TL reading of the annealed but unexposed sample, and M is the TL response of the exposed sample to a test dose. Rejecting the TLDs that are causing the linearity index, Δ_{max}, to exceed the tolerance limit is necessary.

2.2.1(i) Annealing

One way to increase a thermosensitive material's sensitivity or decrease its thermal fading is by applying annealing, a thermal treatment. Pre- and post-irradiation annealing are the two categories into which the annealing is divided. To fully eliminate the residual signal without causing any damage to the dosimetric material, pre-irradiation annealing is necessary, which is often carried out in a furnace or oven, as shown in Figure 2.4. Reduces the sensitivity significantly when annealed at higher temperatures for longer periods. Consequently, to sensitise the recently developed TL material, the annealing parameters must be optimised. Through the stabilisation of the holes and traps, the appropriate annealing process enhances the TL material's sensitivity. High-temperature annealing is generally necessary to eliminate residual signal dosimetric traps, which could otherwise introduce unwanted background noise when a TL dosimeter is used subsequently. Any TL dosimetric material's TL response is highly dependent on the annealing process used. Each TL dosimetric material has a preferred annealing process of its own.

For a TL dosimeter, the ideal annealing process combines the right amount of annealing time and temperature to produce the optimum TL response with the lowest possible STD and respectable repeatability. Since the cooling rate used to bring the TL material down to room temperature post-annealing at a predetermined temperature for a predetermined amount of time greatly influences the TL dosimetric material's sensitivity, a reproducible cooling rate is particularly desirable. Because each TL dosimetric material is different chemically, it requires a different set of annealing parameters. For a TL dosimetry system to be economically efficient, a straightforward annealing procedure is ideal. The typical annealing process for LiF:Mg,Ti is thought to be complex since it involves high-temperature thermal treatment for 1 h at 400 ^{o}C, followed by low-temperature thermal treatment for 2 h at 100 ^{o}C or 20 h at 80 ^{o}C. The main goal of low-temperature annealing after radiation is to eliminate any low-temperature glow peaks ($\leq$ 100 ^{o}C) that may be thermally unstable at room temperature and cause the TL material to fade thermally. The annealing temperature is the only difference between the pre-irradiation and post-irradiation annealing optimisation procedures; in the former case, the TL material is subjected to temperatures higher than the dosimetric peak temperature, while in the latter case, the TL material is subjected to lower temperatures (Furetta, 2003).

Figure 2.4 A programmable electric annealing oven for pre-irradiation annealing (Esu, 2021)

2.2.1(j) Dose Response

Naturally, the TL dose-response is the most crucial feature of TL dosimeters and establishes the dose range within which the dosimeter is usable, subject to dose-response linearity, and should also establish the dose measurement accuracy as a dose function. Numerous TL materials show a dose-response with a low-dose linear region, where the TL signal intensity F, which is typically expressed as the integrated area within a specific temperature range or channel, or as the peak height or area of a specific glow peak, is proportional to the dose, d. Therefore, $F \propto d$ (Horowitz et al., 2007). Dose-response is said to be the functional reliance of calculated TL intensity on absorbed dose. Over a wide dose range, a dosimetric material should ideally show a linear dose-response. However, in practice, a TLD material exhibits linear, supralinear, and sublinear behaviour as the dose is increased (Bakhsh et al., 2018). Eqn. (2.12) provides the supralinearity index, which can be used to ascertain a TLD material's linear dose range.