FUNDAMENTAL PROPERTIES OF COPPER-DOPED AND CO-DOPED SnO₂ OF LITHIUM POTASSIUM BORATE GLASS EXPOSED TO PHOTON BELOW 4GY

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UNIVERSITI TEKNOLOGI MALAYSIA
FUNDAMENTAL PROPERTIES OF COOPER-DOPED AND CO-DOPED SnO₂
OF LITHIUM POTASSIUM BORATE GLASS EXPOSED TO PHOTON BELOW
4GY

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Physics)

Faculty of Science
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This thesis is dedicated to

To my dear parents

To my beloved wife
Aseel Shakir Naij

To my sister
Kuther Aboud Namma

To my siblings
ACKNOWLEDGEMENT

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The glass samples of composition $10K_2CO_3 - (90 - x) H_3BO_3$ with $10 \leq x \leq 30$, $20Li_2CO_3 - 10K_2CO_3 - (70 - x) H_3BO_3 - xCu$ with $0.05 \leq x \leq 1.0$ and $20Li_2CO_3 - 10K_2CO_3 - (69.9 - x) H_3BO_3 - 0.1Cu - xSnO_2$ with $0.05 \leq x \leq 0.2$ have successfully been prepared by melt-quenching technique. The samples were analyzed by X-ray diffraction spectrometer to confirm that the sample is amorphous. The energy band gap measurements of the glass samples reveal that introducing copper into lithium borate glass reduce the energy band gap of the samples, while the addition of SnO$_2$ into Cu-doped sample increase the energy band gap. The impact of SnO$_2$ gives an enhancement in the luminescence intensity by almost 3 times when 0.1 mol% SnO$_2$ was added to 0.1 mol% Cu-doped borate glass. The peaks shapes shifted from blue luminescence to blue and green luminescence for Cu-doped and co-doped samples respectively. The thermoluminescence (TL) properties of Cu-doped and co-doped with SnO$_2$ glass were investigated in this work. The glow curves position of Cu-doped and co-doped with SnO$_2$ glass were recorded at $205^\circ C$ and $215^\circ C$ respectively at a heating rate of $20^\circ C$ s$^{-1}$. In addition, the optimum annealing procedure of Cu-doped and co-doped with SnO$_2$ glass was 20 min at 400 $^\circ C$ and 30 min at 400 $^\circ C$ respectively. The highest TL intensity of Cu-doped sample was recorded at Cu concentration of 0.1 mol%. The highest TL intensity for co-doped with SnO$_2$ glass was observed at SnO$_2$ concentration of 0.1 mol%. The linear relationship of dose–TL intensity was observed for both glass samples for different doses ranging from 0.5 to 4.0 Gy subjected to 6, 10 and 12 MV X-ray photon energies and Co-$\gamma$-60 gamma ray. The co-doped with SnO$_2$ glass has always higher TL response compared to Cu-doped glass. The study of fading characteristics shows that co-doped with SnO$_2$ glass has lower fading compared to Cu-doped glass. Reproducibility study of both types of glasses show the thermoluminescence intensity of Cu-doped glass are slowly decreasing about 1.6% with the repeating readout and about 1.3% for co-doped with SnO$_2$. Study on the TLD sensitivity shows that the co-doped with SnO$_2$ glass is almost 6 times more sensitive than the Cu-doped glass. The TL sensitivity was found as 75 $\mu$C g$^{-1}$Gy$^{-1}$ and 266 $\mu$C g$^{-1}$Gy$^{-1}$ for Cu-doped and co-doped with SnO$_2$ glass respectively. The relative energy response of Cu-doped and co-doped with SnO$_2$ glass have been calculated theoretically for photon energies up to 1.25 MeV and it is found that the theoretical calculations are in good agreement with the experimental results. The average value of activation energy and the average frequency of Cu-doped and co-doped with SnO$_2$ glass are calculated.
ABSTRAK

Sampel kaca dengan komposisi $10K_2CO_3 - (90 - x) H_3BO_3$ dengan $10 \leq x \leq 30$, $20Li_2CO_3 - 10K_2CO_3 - (70 - x) H_3BO_3 - xCu$ dengan $0.05 \leq x \leq 1.0$ dan $20Li_2CO_3 - 10K_2CO_3 - (90 - x) H_3BO_3 - 0.1Cu - xSnO_2$ dengan $0.05 \leq x \leq 0.2$ telah berjaya dihasilkan menggunakan teknik pelindapan lebur. Sampel dianalisis menggunakan spektrometer pembelauan sinar-X bagi mengesahkan sampel adalah amorfus. Pengukuran jurang jalur tenaga menunjukkan bahawa penambahan unsur kuprum ke dalam sampel kaca litium borat mengurangkan jurang jalur tenaga, manakala jurang jalur tenaga meningkat selepas SnO_2 ditambah dalam sampel kaca. Impak SnO_2 meningkatkan keamatan luminesens kepada hampir tiga kali ganda apabila 0.1 mol% SnO_2 ditambahkan kepada kaca borat yang didopkan dengan 0.1 mol% Cu. Bentuk puncak masing-masing teranjak daripada luminesens biru kepada luminesens biru dan hijau bagi kaca yang didopkan dengan Cu dan diko-dop dengan SnO_2. Ciri termoluminesen (TL) bagi sampel yang didop dengan Cu dan yang diko-dop dengan SnO_2 dikaji dalam kajian ini. Kedudukan puncak masing-masing teranjak dari pada suhu 205°C dan 215°C pada kadar pemanasan 20°C. Kaca yang diko-dopkan dengan SnO_2 sentiasa mempunyai respon TL yang lebih tinggi berbanding dengan kaca yang didopkan dengan Cu. Kajian ciri kepudaran menunjukkan kaca yang diko-dopkan dengan SnO_2 mempunyai sifat kepudaran yang lebih baik berbanding dengan kaca yang didopkan dengan Cu. Kajian kebolehgunaan semula bagi kedua-dua jenis kaca menunjukkan keamatan TL bagi kaca yang didopkan dengan Cu berkurang secara perlahan kira-kira 1.6% dan 1.3% bagi kaca yang diko-dopkan dengan SnO_2. Respon tenaga relatif bagi kaca yang didopkan dengan Cu dan diko-dopkan dengan SnO_2 telah dikira secara teori bagi tenaga foton sehingga 1.25 MeV dan didapati nilai teori mempunyai persamaan yang sama dengan keadaan eksperimen. Nilai purata kepekaan masing-masing adalah 75 μCg^{-1}Gy^{-1} and 266 μCg^{-1}Gy^{-1} bagi kaca yang didopkan dengan Cu dan yang diko-dopkan dengan SnO_2. Respon tenaga relatif bagi kaca yang didopkan dengan Cu dan diko-dopkan dengan SnO_2 telah dikira secara teori bagi tenaga foton sehingga 1.25 MeV dan didapati nilai teori mempunyai persamaan yang sama dengan keadaan eksperimen.
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<tr>
<td>$Be$</td>
<td>The binding energy of the electron</td>
</tr>
<tr>
<td>$C$</td>
<td>Coulomb</td>
</tr>
<tr>
<td>$D$</td>
<td>Absorbed dose</td>
</tr>
<tr>
<td>$D_o$</td>
<td>Threshold dose</td>
</tr>
<tr>
<td>$E$</td>
<td>Trap depth</td>
</tr>
<tr>
<td>$Ef$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>$E_{fg}$</td>
<td>Forbidden energy</td>
</tr>
<tr>
<td>$E_{max}$</td>
<td>The maximum energy</td>
</tr>
<tr>
<td>$E_{Y}$</td>
<td>Energy of the incident photon</td>
</tr>
<tr>
<td>$E_{Y'}$</td>
<td>Energy of the scattered photon</td>
</tr>
<tr>
<td>$F$</td>
<td>TL system calibration factor</td>
</tr>
<tr>
<td>$Gy$</td>
<td>Gray</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$Li$</td>
<td>Lithium</td>
</tr>
<tr>
<td>$LiF$</td>
<td>Lithium fluoride</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>$m_0$</td>
<td>The electron rest-mass</td>
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<tr>
<td>$n$</td>
<td>Number of electrons in a particular trap energy</td>
</tr>
<tr>
<td>$n_o$</td>
<td>The number of trapped electrons at the initial time</td>
</tr>
<tr>
<td>$p$</td>
<td>Probability of escaping by the trap</td>
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<tr>
<td>$RER$</td>
<td>Relative Energy Response</td>
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<td>$SnO_2$</td>
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<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$TL$</td>
<td>Thermoluminescence</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>TLD</td>
<td>Thermoluminescence dosimeters</td>
</tr>
<tr>
<td>$w_i$</td>
<td>Fraction of that element</td>
</tr>
<tr>
<td>$Z$</td>
<td>Atomic number of the atom</td>
</tr>
<tr>
<td>$Z_{\text{eff.}}$</td>
<td>Effective atomic number</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Half-life of the phenomenon</td>
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CHAPTER 1

INTRODUCTION

1.1 Overview

Thermoluminescence (TL) is a luminescence phenomenon of an insulator or semiconductor which can be observed when the solid is thermally stimulated. TL process should not be confused with the light spontaneously emitted from a substance when it is heated to incandescence. At higher temperatures a solid emits (infra) red radiation of which the intensity increases with increasing temperature. This is thermal or black body radiation. TL, however, is the thermally stimulated emission of light following the previous absorption of energy from radiation. From this description the three essential ingredients necessary for the production of TL can be deduced. Firstly, the material must be an insulator or a semiconductor metals do not exhibit luminescent properties. Secondly, the material must have at some time absorbed energy during exposure to ionizing radiation. Thirdly, the luminescence emission is triggered by heating the material (McKeever, 1985). The stored energy is released in the form of visible light when the material is heated.

The first description of thermoluminescence was given by Boyle on 28 October 1663, where he observed strange ‘glimmering light’ when he warmed a diamond in the darkness of his bedroom. Oldenberg, in 1705 described the phenomenon of thermoluminescence in mineral and fluorite. He also described other properties of such phosphors. In 1883, Pearsall gave a description of the effects of electricity upon minerals which luminescence upon heating. Becquerel described in
his work the effect of thermoluminescence on measurement of infrared spectra in 1883. Wiedemann and Schmidt, in 1895, used the physical process for the thermal release of stored radiation induced luminescence (thermoluminescence) for the detection of ionizing radiation. In 1925, Wick, from Vassar College described the effects of X-ray in modifying and producing thermoluminescence. Many researchers have benefited from this phenomenon and have used it in many applications (Becker, 1973).

Daniels and his co-workers in the late 1940s, used thermoluminescence to make quantitative measurements of radiation exposure, for example, examining the glow peak structure and isothermal fading of alkali halides. They concluded that lithium fluoride (LiF) from Harshaw Chemical Company was most suitable for measuring ionizing radiation exposure. For some studies of LiF in 1960, Harshaw incorporated titanium and other elements in the LiF to produce phosphor with high TL sensitivity. This material is the basis of what is now generally regarded as the ‘standard’ TL phosphor: Harshaw TLD 100 (McKinlay, 1981).

Nakajima et al. (1978) described the preparation and properties of a highly sensitive LiF dosimetry, incorporating Mg, Cu, and P as dopant. Mg and Cu doping alone gives the ‘usual’ emission near 410 nm, but the addition of P increases emission at 340 nm (Oberhofer, 1981).

Now, there are a few commercially available thermoluminescence dosimeters (TLD). LiF: Mg, Ti (TLD–100), LiF: Mg, Cu, P (TLD–700H), Li2B4O7: Cu, Ag, P (TLD–800), CaSO4: Dy (TLD–900), CaF2: Dy (TLD–200) and Al2O3 (TLD–500) as examples of the commercially thermoluminescence materials (Driscoll et al., 1984, Fox et al., 1988 and Noh et al., 2001). Extensive research is being carried out to improve their dosimetric properties (Sahare et al. 1990, Dhoble et al., 1993, Prokic, 2001, Lakshmanan et al., 2002, Shinde et al., 2001 and Kim et al., 2004). Most of the commercial thermoluminescence dosimeters are polycrystalline, as they can be manufactured with ease (McKeever et al., 1995).
Dosimetric materials have to have some specific properties that all thermoluminescence dosimeters are expected to fulfill. These specific features can be given as follows (Pradhan, 1981, Furetta et al., 1999; 2001 and Kortov, 2007).

i) A thermoluminescence dosimeter should give a simple and single glow peak around (180–250 °C). If several glow peaks are present, at least the main peak should be well resolved. However, for this type of thermoluminescence dosimetry, dosimeter heating protocol is complicated.

ii) The dosimeter should have high gamma ray sensitivity. High sensitivity is important especially for use in personnel and medical dosimetry. The dosimeter is expected to have high response per unit of absorbed dose.

iii) Dosimeters ought to have low fading property which is the ability to store dosimetric information for a long time.

iv) The thermoluminescence dosimeter should be mechanically strong, resistant against humidity, gases, moisture, and organic solvents.

v) The thermoluminescence material should have high light resistivity.

vi) Especially for thermoluminescence dosimeter used in personnel and medical dosimetry, it should has effective atomic number close to that of the human tissue.

vii) The luminescence spectrum should match the maximum spectral sensitivity of the photomultiplier.

viii) The thermoluminescence materials should able to be reused several times and they should have simple annealing process.

ix) They must be cheap and non-toxic in case of in-vivo use.

However, all the commonly used phosphors do not have all the above stated characteristics at one shot, it will not be ideal (Salah et al., 2007, Kortov, 2007 and Berger et al., 2008). For example, CaSO₄: Dy has a good sensitivity but poor tissue equivalence. Its effective atomic number is 16.7 (Spurny, 1980 and Lakshmanan, 2001). On the other hand, LiF-TLD 100 is tissue equivalent but it has a poor TL
response. Its TL response is nearly ten times less than that of CaSO$_4$: Dy (Salah et al., 2007). In addition, LiF compound has a complex glow curve (Horowitz, 1984) and LiF: Mg, Cu, P is very sensitive to thermal treatments (Barbina et al., 1981). MgB$_4$O$_7$: Dy/Tm exhibits high batch to batch variation (Mahesh et al., 1989). Li$_2$B$_4$O$_7$: Mn has low sensitivity (Busuoli et al., 1977) and Li$_2$B$_4$O$_7$: Cu has high optical fading (Prokic, 1980) and they have poor reproducibility (Mc Keever et al., 1989), BeO has high fluctuation of the TL signal at low doses (Prokic 1993). Li$_2$SO$_4$: P, Dy and Li$_2$SO$_4$: Eu phosphors have high effective atomic ($Z_{eff}$=11.19) number (Dhoble et al., 2003). Therefore, research is going on to prepare new phosphors with better TL characteristics or to improve the existing dosimetric materials, for instance, B$_2$O$_3$–Li$_2$O: Mg glass (Elkholy, 2010), Li$_2$B$_4$O$_7$:Cu single crystals (Tiwari et al., 2010), Li$_2$B$_4$O$_7$:Mn, Ag, P and Mg (Kayhan et al., 2011), CaSO$_4$: Dy or Tm: Li co-doped (Wang et al., 2011) and Li$_2$B$_4$O$_7$:Cu, Ag, In (Pekpak et al., 2011).

1.2 Statement of the Problem

Dosimetric materials should have several characteristics like near tissue equivalence, excellent stability, high sensitivity, simple glow curve structure which is ideally a single glow peak at about 200°C and simple annealing procedure for reproducibility. There are some dosimetric materials which are used in industry and also a lot of new compounds produced by researchers, but none of them have all the above stated properties. Therefore, there have always been attempt to either prepare new dosimetric materials with better thermoluminescence characteristics or simply improve upon the already existing dosimetric materials by varying the concentration of the impurities or by co-doping of the phosphor with other elements or doping new impurities in new matrices. This research focused on the study of Cu dopes and co-doped of SnO$_2$ nanoparticle of lithium potassium borate glass as TL material subjected to photons and Co-60 gamma ray. This study is concerned with the linearity of dose-TL response relationship, fading characteristics, energy response, sensitivity, optical bleaching, reproducibility and dose threshold.
1.3 **Objectives of the study**

The objectives of the research are as follows:

1. To prepare and determine the optical properties of Cu-doped lithium potassium borate glass and co-doped SnO$_2$ nanoparticles of Cu-doped lithium potassium borate glass.

2. To study the optimum setting of TLD Reader such as annealing temperature and heating rate for the sample under investigation.

3. To investigate the fundamental thermoluminescence properties of Cu-doped lithium potassium borate subjected to 6, 10 and 12 MV photon and Co$^{60}$ gamma irradiation.

4. To investigate the fundamental thermoluminescence properties of co-doped SnO$_2$ nanoparticles of Cu-doped lithium potassium borate subjected to 6, 10 and 12 MV photon and Co$^{60}$ gamma irradiation.

1.4 **Scope of the Study**

This work may provide a principle for employing TL phenomena in several dosimetric situations. Two types of samples were prepared in this work, i.e. Cu-doped and co-doped SnO$_2$ nanoparticles of lithium potassium borate glass. Their general properties, which include linearity, energy response, reproducibility, re-use and fading characteristics, sensitivity and effective atomic number, may provide doped and co-doped lithium potassium borate glass for the introduction of new TL material. These samples may be useful for several of applications especially in radiation therapy.
The irradiation on the doped and co-doped lithium potassium borate glass systems have been conducted at different dose levels from 0.5–4.0 Gy of ionizing radiation sources. These samples were irradiated with 6, 10 and 12 MV photon beams and $^{60}$Co gamma ray. Moreover, this present work has also been carried out to determine the effective atomic number, $Z_{\text{eff}}$ of doped and co-doped lithium potassium borate glass systems using a scanning electron microscope (FE-SEM).

This thesis contains 5 Chapters. **Chapter 1** provided an introduction to the phenomenon associated with TL mechanism, offered the objective of the study and statements of hypotheses. **Chapter 2** addresses the mathematics of thermoluminescence and methods of analyzing the TL glow curve. This chapter also discussed several method of analysis to calculate the values of kinetic parameters (activation energy, $E$ and frequency factor, $s$). Important TL characteristics were highlighted including annealing condition; glow curves parameters, energy dependence, relative energy response, dose rate effect, heating rate effect and optical bleaching. **Chapter 3** describes the methodology and procedures in samples preparation. In addition, it also explain all the equipments used in this study. In **Chapter 4**, the results obtained are presented and discussed in details. **Chapter 5** summarizes the findings of this investigation, and provides an outlook for future studies in this area.
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