UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND EVALUATION OF UNDOPED AND SILVER AND COPPER DOPED LITHIUM TETRABORATE NANOPARTICLES AS THERMOLUMINESCENCE DOSIMETER

NASRIN KHALILZADEH

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By

NASRIN KHALILZADEH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

August 2014

DEDICATION

This Thesis is dedicated to my beloved husband, Majid, and my sweetheart son, Danial, who have supported and encouraged me all the way since the beginning of my PhD studies at UPM. Since without their encouragements, I would never be able to accomplish my research. Besides, a special thanks goes to my husband's parents Mr. and Mrs. Mirabolghasemi and my brothers' in law Hadi, Majd, and Dr.Hamed, who like their parents were more than generous with their precious time to give me spiritual supports and encouragements. I feel I am spiritually in debt of my husband's family, and to the memory of my parents who were motivated me for learning through my life journey. Finally, this thesis is dedicated to all those who believe in the richness of learning.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS AND EVALUATION OF UNDOPED AND SILVER AND COPPER DOPED LITHIUM TETRABORATE NANOPARTICLES AS THERMOLUMINESCENT DOSIMETER

By

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August 2014

Chairman: **Professor Elias B Saion, PhD**

Faculty: **Science**

Tissue equivalent thermoluminescence dosimeters (TLDs) are commonly used for monitoring dose of ionizing radiation as personal or medical radiation dosimeters. The commercially available macro-scale lithium tetra borates (LTB) have several drawbacks such as poor Thermoluminescent (TL) intensity, limited dose linearity, losses information with time (fading) and energy dependence, which might be improved by using nano-scale activated LTB, the main goal of this study. LTB is the most popular material for radiation dosimetry because of its effective atomic number (Z_{eff} = 7.4) that close with the Z_{eff} of human tissue (7.42). Furthermore, LTB is almost stable chemical compound and can be easily doped with TL sensitizers. In line with this development the objectives of this work were to synthesize and to investigate the structural characteristics and TL properties of undoped LTB and silver and copper doped LTB (LTB-Ag and LTB-Cu) nanoparticles for dosimetric applications. The LTB nanoparticles were synthesized by using innovative single step thermal treatment method. Subsequently, the samples were investigated for thermal stability and phase transition using thermal gravimetric analysis (TGA), derivative thermogravimetry analysis (DTG), and differential scanning calorimetry (DSC). The TGA, DTG, and DSC results showed the triple phases of mass loss were observed. Fourier transform infrared spectroscopy (FT-IR) was used to monitor the formation nanoparticles in the range of 200-4000 cm^{-1}. The samples were subjected to different calcination temperatures and found 650, 700, and 750 ^oC were the principal calcination temperatures based on the X-ray diffraction

(XRD) patterns and transmission electron microscopy (TEM) images. To study the effect of PVP capping agent for regulating nanoparticles' agglomeration, 0.009, 0.018, and 0.027 mol of PVP concentrations were used. The narrowest particle size and size distributions were reached at 0.027 mol of PVP for LTB and LTB-Cu nanoparticles and at 0.018 mol of PVP for LTB-Ag nanoparticles. The average particle sizes determined from TEM size distributions were 3.34, 4.61, and 4.56 nm for LTB, LTB-Cu and LTB-Ag nanoparticles, respectively at calcination temperature of 750 ^{o}C. The UV-visible spectroscopy (UV-Vis) was used to determine the optical bandgap of the synthesized nanoparticles. To investigate the TL property of the synthesized nanoparticles, dose response, energy storage ability, and energy dependence of nanophosphors were studied from glow curve of dose response at a variety of dose ranges of 0.005, 0.01, 0.1, 0.5, 1, 10, 100, and 150 Gy. The current nano-scale doped and undoped LTB dosimeters have good physical properties and TL response that they can be produced easily by single step thermal treatment method at effective cost and without by-product effluents.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBUATAN DAN PENILAIAN TIDAK TERDOP DAN TERDOP NANOPARTIKEL LITHIUM TETRA BORAT OLEH PERAK DAN TEMBAGA SEBAGAI DOSIMETER TERMOPENDARKILAU

Oleh

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Tisu dosimeter termopendarkilau setara (TLD) biasanya digunakan untuk memantau dos radiasi mengion sebagai dosimeter radiasi peribadi atau perubatan. Litium tetra borat berskala makro (LTB) boleh didapati secara komersial dan mempunyai beberapa kelemahan seperti keamatan TL rendah, kelinearan dos terhad, kehilangan maklumat dengan masa (pudar) dan pergantungan tenaga, ia boleh diperbaiki dengan menggunakan skala-nano yang diaktifkan LTB, yang merupakan matlamat utama kajian ini. LTB adalah bahan yang paling popular untuk dosimetri radiasi kerana keberkesanan nombor atom (Zeff = 7.4) yang menghampiri dengan Zeff tisu manusia (7.42). Tambahan pula, LTB adalah sebatian kimia yang hampir stabil dan mudah didopkan dengan pemeka TL. Selaras dengan perkembangan ini objektif kerja ini adalah untuk mensintesis dan untuk menyiasat ciri-ciri struktur dan sifat-sifat TL yang diadapati daripada nanopartikel LTB tidak terdop dan LTB terdop perak dan tembaga (LTB-Ag dan Cu-LTB) untuk aplikasi dosimetrik. Nanopartikel LTB telah disintesis dengan menggunakan langkah inovatif kaedah rawatan haba. Selepas itu, sampel telah disiasat untuk kestabilan terma dan peralihan fasa menggunakan analisis terma gravimetrik (TGA), analisis termo terbitan (DTG), dan kalori pengimbasan kebezaan (DSC). Keputusan TGA, DTG, dan DSC menunjukkan tiga fasa kehilangan jisim telah diperhatikan. Spektroskopi pengubah fourier inframerah (FT-IR) telah digunakan untuk memantau pembentukan nanopartikel dalam lingkungan 200-4000 cm-1. Sampel telah diselaraskan kepada suhu pengkalsinan yang berbeza dan didapati 650, 700, dan 750 ^{o}C adalah suhu pengkalsinan utama berdasarkan pembelauan corak sinar-X (XRD) dan penghantaran imej mikroskop elektron (TEM). Untuk mengkaji kesan ejen penetapan polimer PVP bagi mengawal selia penumpuan nanopartikel, berkepekatan 0.009, 0.018, 0.027 mol PVP digunakan. Saiz zarah sempit dan saiz agihan telah dicapai pada 0.027 mol PVP untuk nanopartikel LTB dan LTB-Cu dan pada 0.018 mol PVP untuk nanopartikel LTB-Ag. Saiz purata zarah ditentukan dari taburan saiz TEM adalah 3.34, 4.61, dan 4.56 nm untuk nanopartikel LTB, LTB-Cu dan LTB-Ag, masing-masing pada suhu pengkalsinan 750 ^{o}C. Spektroskopi UV-tampak (UV-Vis) telah digunakan untuk menentukan pemberian nilai jurang optik nanopartikel yang disintesis. Untuk menyiasat kandungan TL daripada nanopartikel disintesis, pergantungan dos, keupayaan penyimpanan tenaga, dan tenaga nanophosphors dikaji dari lengkung cahaya tindak balas dos di pelbagai julat dos 0.005, 0.01, 0.1, 0.5, 1, 10, 100 , dan 150 Gy. Kini dosimeter LTB berskala nano terdop dan tidak terdop LTB mempunyai ciri-ciri fizikal yang baik dan tindak balas TL boleh dihasilkan dengan mudah oleh rawatan terma pada kos yang berpatutan dan tanpa dipengaruhi oleh produk dihasilkan.

ACKNOWLEDGEMENTS

In the name of Allah the merciful Beneficent

I wish to express my sincere appreciation to Prof. Elias Saion who has taught me so much about nanoscience, with whom I began teaching nanotechnology. His knowledge, graciousness, and wisdom will be forever memorable to me.

Moreover, I wish to thank my committee members with gratitude; Prof. Abdul Halim B Shaari, Prof. Mansor B Hashim, Prof. Mansor B HJ Ahmad, and Dr. Noriah Mod Ali for their suggestions, consideration and support through my graduate career. I acknowledge with gratitude Prof. Karen whose grate consideration grew my chemistry knowledge and spirituality as well. I acknowledge Prof. Azmi, Prof. Halimah, and Prof. Jumiah for their kindness and graceful help. I greatly appreciate and wish to thank Mr. Mohd Zain Yusof for his immense help and the Faculty of Science, Physics department lecturers and staff, Institute Bioscience, Faculty of Engineering, and Institute of Advance Technology (ITMA), of University Putra Malaysia, who had contributed to this research. Special thanks to librarians who generally patiently gave me a hand, particularly Jefri who was always there to help, SGS staff who informed and guided me through formal procedures. I acknowledge with gratitude the staff of the Agency Nuclear Malaysia and University Kebangsaan Malaysia who made my work possible.

Besides, a special thank to my lovely friends, Saghi and Afsane who encouraged me to come to UPM, Dr. Mirzaee and Dr. Karimian who believed in me and supported me, Mr. Ghafoori and Dr. Zamani who trust me and made my educational mission possible, Maryam and her sister, Mehrnaz who helped me compassionately. Finally, great thanks to my lovely friends, Saeed and Neda who were accessible all the time days or nights to help me thousands kilometers away, wish you all the best in your life.

Nasrin Khalilzadeh

August 2014

This thesis submitted to the Universiti Putra Malaysia and has been accepted as fulfillment of the requirements for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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CHAPTER 1

INTRODUCTION

1.1 Nanostructured materials

Ultrafine structures having an average phase or grain size the order of 10^{-9} m are classified as nanostructured materials (NSMs) (Gleiter, 1992). Currently, in a wider meaning of the term, any material that contains grains or clusters below 100 nm, or layers or filaments of that dimension, can be considered as "nanostructured" (Seigel, 1993a). The interest in these materials has been stimulated by the fact that, owing to the small size of the building blocks (particle, grain, or phase) and the high surface-to-volume ratio, these materials are expected to demonstrate unique mechanical, optical, electronic, and magnetic properties (Seigel, 1993b). The properties of NSMs depend on the following four common microstructural features; (1) fine grain size and size distribution(< 100 nm), (2) the chemical composition of the constituent phases, (3) the presence of interfaces, more specifically, grain boundaries, heterophase interfaces, or the free surface, and (4) interactions between the constituent domains. The presence and interplay of these four features together with their combined electronic structure largely determine the unique properties of NSMs. In nanophase materials, a variety of size-related effects can be incorporated by controlling the sizes of the constituent components (Chan, 1990). For example, nanostructured metals and ceramics show improved mechanical properties compared to conventional materials as a result of their ultrafine microstructure. In addition, NSMs have the capability to be sintered at much lower temperatures than conventional powders, enabling the full densification of these materials at relatively lower temperatures. Semiconductor NSMs are currently also considered to have technological applications in optoelectronic devices such as semiconductor quantum dots and photodiodes, owing to the phenomenon of "quantum size effects" caused by the spatial confinement of delocalized electrons in confined grain sizes (Wang, 1991). Magnetic applications of NSMs include fabrication of devices with giant magnetoresistance (GMR) effects, the property used by magnetic heads to read data on computer hard drives, as well as the development of magnetic refrigerators with solid magnets as refrigerants rather than compressed ozone-destroying chlorofluorocarbons (Yoshizawa, 1988). In addition, nanostructured metals and alloy seem to be candidates for new catalytic applications (Beck, 1992).

The development of semiconductor nanoclusters is an area of intense research efforts. These nanoclusters are often referred to as quantum dots and nanocrystals (Steigerwald, 1990). In the nanometer size regime, electron-hole confinement in nanosized spherical semiconductor particles results in three-dimensional size quantization. Bandgap engineering by size and dimension quantization is important as it leads to electrical, optical, magnetic, optoelectronics, and magnetoptical properties substantially different from those observed for the bulk material (Henglein, 1988). As an example, quantum dots can be developed to emit and absorb a desired wavelength of light by changing the particle diameters. This feature allows the construction of a finely tunable and efficient semiconductor laser (Gonsalves, 2000).

1.2 Lithium borate Crystals

The lithium borate crystals LiB_3O_5 (LBO), $Li_2B_4O_7$ (LTB), $Li_6Gd\ (BO_3)_3$ (LGBO) are typical representatives of an extensive class of wide band-gap dielectrics with mobile cations. Recently these optical materials have been intensively investigated from both the point of view of their fundamental properties, and with respect of their practical application in fields of radiation detectors (Furetta, 2010), dosimetry (Ignatovych, *et al.*, 2004), transformers and optical wave-guides operating in a broad spectral range from the visible region to the vacuum ultraviolet region (Ogorodnikov, *et al.*, 2012). All the crystals are highly transparent down to the cutoff wavelength near 160 nm and their band gaps are estimated to be 8.8–9 eV (Ogorodnikov, 2010). The lithium borate crystals have recently become promising candidates for the realization of neutron imaging using scintillation methods (AM, 2004). Despite variations in chemical composition, these materials have many similar properties. In particular, they have a reduced symmetry of the crystal lattice and a complex elementary cell. The crystal structure of each material consists of the appropriate boron-oxygen anionic groups and lithium cations. The lithium cations occupy the voids in the continuous boron-oxygen network. A distinctive feature of these materials is the sharp contrast between the strong covalent chemical bonds inside the anionic groups and the comparatively weak ionic bonds between the lithium cations and appropriate anionic groups (Islam, 2011; Wooten, *et al.*, 2010).

Lithium tetraborate is one of the selected materials for personal thermoluminescence dosimetry as its effective atomic number (Z_{eff} =7.4) closely matches the Z_{eff} of human tissue (7.42) (Furetta, *et al.*, 2001). The borates are brilliant compounds as a TLD due to their close tissue-equivalent properties. Furthermore, they have an almost stable chemical composition and can be doped with TL sensitizers such as rare earth elements, copper or manganese ions without significant problems. The resultant materials show some desirable features for TL in terms of high sensitivity (El-Faramawya, *et al.,* 2000). However, the conventional macro-scale LTB has several drawbacks such as poor TL intensity, limited dose linearity, loss information (fading) and energy dependence. Takenega et al. (1980) replaced Mn with Cu to improve the sensitivity of LTB. They found that TL emission spectra at 365 nm for LTB: Cu, In pellets and LTB: Cu, In, Ag pellets improved the linearity of dosimeter however, those TLs are sensitive to light with a high amount of fading (Prokic, 2001). Thereafter, doping of LTB crystals have received attention as a promising method to produce neutron scintillator with large cross sections for neutron capturing by lithium and boron isotopes (Huy, 2009) in surface acoustic wave devices for intermediate frequency (IF) filters (Senguttuvan, *et al.,* 2002), (Lewis, *et al.,* 1982). Furthermore, the dose range of traditional phosphors does not exceed normally 100 Gy, while higher doses are needed in technological and medical applications. In this connection, nanosized phosphors captured the interest of some researchers because of their better radiation resistance (Banhart, 1999; Uzsaki *et al.,* 2007). Over the past few years nanophosphors have been studied actively, leading to some promising results (Chopra, *et al.,* 2013). Therefore, the LTB based TL materials still attract extensive attentions, due to their attractive properties.

1.3 Problem Statement

One of the most important missions in TL dosimetry investigation is invention of new detector materials for radiation monitoring. LTB has been a popular and significant starting material in this regard for a long time (Schulman, *et al.,* 1965).
The TLD material needs to be tissue equivalent and highly sensitive. Moreover, the sizes of TLD materials are required to be as small as possible for lab measurements. Besides, the TLD should not be toxic. Therefore, because of the importance of the tissue equivalent factor, the International Commission on Radiological Protection (ICRP) has published recommended diagnostic reference levels for medical imaging modalities (ICRP, 1996).

Luminescence detectors of ionizing radiation are now comprehensively used in individual dosimetry services due to their excellent dosimetric properties. The most frequently used personal dosimeters are based on optically stimulated luminescence (OSL), radio photoluminescence (RPL) or thermoluminescence (TL). Luminescence detectors have also been applied in clinical dosimetry, especially around new radiation modalities in radiotherapy, such as Intensity Modulated Radiotherapy (IMRT) or ion beam radiotherapy (Olko, 2010).

Although, un-doped LTB crystals show TL emission and its energy dependence is low its sensitivity is much lower than the common detector materials. The idea of adding an activator material came. Thus, a lot of other efforts were made for finding dopants and possible co- doping of LTBs for better TL properties (Patra, *et al.,* 2012; Tiwari, *et al.,* 2010). It is shown by some researchers that some transition metals such as Cu, Ag, Ni, and Co reduced the known drawbacks of LTBs (Ignatovych, *et al.,* 2004; Prokić, 2000). Furthermore, In and Ce was applied as activators to enhance key factors of TL dosimeters (Senguttuvan, 2002). Due to very early in the 1960s Schulman et al. synthesized LTB: Mn for dosimetric purposes. The doped LTB with Mn shows a bit higher sensitivity, but the emission of the material is in the red region that is not favorable for the light detecting systems of the commonly used TL readers (Schulman and Kirk, 1965)o superior results of Cu containing detectors, it becomes the preferred dopant element among other transition elements. This detector showed emission in near UV region (Takenaga, *et al.,* 1980). Comparing to LTB:Mn, the emission of LTB:Cu is more desirable and much better for using with normal TL readers (Azorin, 2013). On the other hand, powder form of LTB: Cu is not wanted for routine application in dosimetry. It should be emphasized that the color of almost all of the commercially prepared lithium borates doped by Cu change (to brownish) after repeated annealing steps (Furetta, *et al.,* 2001).

The mechanism of energy excitation resulting in light emission is the most important point in TL materials sketching. Both the threshold detection dose and validity of measurements depend on the sufficianiency of energy transformation. The impact of diverse procedures of energy transfer and energy losses is very different arising from the nature of the TL substance and its composition including intrinsic defects and those induced by impurities. The amount and distribution of these defects can be controlled to a high extent by the synthesis technique. That is why the most significant fact is to find the interdependence of the preparation methods, the structural defects and the TL properties of the material. Although, there are lots of TL materials, the majority of them are not convenient to be employed for dosimetric purposes. The following characteristics are expected from a good material;
Almost a simple glow curve with the main peak at about 200 ^{o}C, high sensitivity and stability, persistence to environmental factors, independence of the radiation energy, and sufficient linearity in the specific appropriate range of dose.
Only a few materials have been synthesized so far which meet all the above requirements. However, investigation in this field is ongoing and more appropriate TL materials are to be synthesized in the near future.

1.4 Significance of the study

Most of the ionizing radiation that people are exposed in their day-to-day activities come from natural and man-made resources such as invisible radiation from the sky, the ground, the air, and even from food and drink. Such "ionizing" radiations have been utilized in different applications; doctors use X-rays to diagnose diseases or injuries; factories use radiation to check welds in machine components; gamma rays are used to sterilize medical equipments for safe use; and a variety of crops have been produced through radiation-induced mutations. Moreover, about 17 percent of the world's electricity is supplied by nuclear power plants.

Natural and artificial health effects of radiation are both well understood and can be effectively minimized through careful safety measures and practices. The International Atomic Energy Agency (IAEA), together with other international and expert organizations is helping to promote and institute Basic Safety Standards (BSS) on an international basis to ensure that radiation resources and radioactive materials are managed to work under maximum safety, human benefit, and environment protection (IAEA, 2011). Due to the extensive application of ionizing radiation, monitoring is the first and the best intervention to confine the hazards of radiation (IAEA, 1999). In order to secure the personal and the environment, massive investigations have been done to synthesize new materials for dosimetric purposes.

The present study reports for the first time, the properties of LTB, LTB-Cu, and LTB-Ag nano phosphors in pellet form, synthesized through an innovative single step thermal treatment method. The prepared pellets were then employed as a new material to improve linearity, energy storage ability, and energy dependence on microcrystalline material as dosimeters. In the present research, nanophosphors are synthesized from aqueous solutions of metal carbonate, Polyvinylpyrrolidone (PVP), copper (II) and silver nitrate as dopants, and Di-water as solvent at a low calcination temperature followed by grinding and sieving. The proposed method is a less expensive route compared to other methods resulting in a pure production without any toxic material which can be mass produced.

1.5 Objectives of the study

The present research is targeted to synthesize un-doped Lithium tetra borate and doped LTB nanophosphors with Cu and Ag by an innovative single step thermal treatment method. To reach to the determined goals, the objectives of the present study are:

1. To synthesize of LTB, LTB-Cu, and LTB-Ag (LTBs) nanophosphors using single step thermal treatment method.

2. To determine thermal stability, crystal structure, optical properties, size and size distribution of prepared nanoparticles.

3. To investigate the effect of PVP concentration on prepared nanophosphores.

4. To investigate the influence of calcination temperature on prepared nanophosphores.

5. To study some main dosimetric properties of achieved LTB, LTB-Cu, and LTB Ag nanophosphors.

1.6 Outline of the Thesis

The foremost aim of the present thesis was to develop a single step thermal treatment synthesis and investigate the physical properties of un-doped and doped LTB nanophosphors and their TLD performance as dosimeters for personal, environmental, and medical purposes.

In Chapter 1 detailed definitions and introductions into the context of the research, purposes, and objectives of the investigation are given. Chapter 2 describes the background of the Thermoluminescence and its role in ionizing radiation dosimetry, followed by a general introduction to LTB crystals and a detailed review of $Li_2B_4O_7$ crystal, its dopant materials, and synthesis methods. As TLDs are prepared in nano regime, Chapter 2 also discusses the properties of the nanostructured materials. Chapter 3 depicts the theory of luminescence and thermoluminescence, energy bands and localized level in crystalline materials. Moreover, the transmission phenomenon is introduced in Chapter 3. The experimental methods and procedures including materials and chemicals chosen to perform the research work are given in Chapter 4. The fallowing chapter (Chapter 5) presents the details of the experimental results and analyses. And finally the conclusion is offered in Chapter 6.

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