

UNIVERSITI TEKNOLOGI MARA

**STRUCTURE AND OPTICAL
PROPERTIES OF SiO₂-ZrO₂ DOPED
Er³⁺ IONS THIN FILMS AND
NANOFIBRES**

NURUL FASIHAH BINTI MOHD SUHAIMI

Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science
(Physics)

Faculty of Applied Sciences

November 2017

ABSTRACT

The thin film samples in the composition of $(100-x)\text{SiO}_2-(x)\text{ZrO}_2$ doped 0.58 mol% Er^{3+} with x varies from 30 mol% to 70 mol% were prepared via sol-gel dip coating technique, meanwhile the nanofibres were prepared using electrospinning technique. All the thin film samples were characterized for morphological, optical and structural properties while the nanofibres samples were characterized based on the morphological and optical properties. The AFM results of the thin film samples showed that the surface morphology were crack-free with compact and uniform structure. The thickness, surface roughness and refractive index of the thin film samples increases as the x mol% increase, meanwhile the transparency of the films reduced. The XRD results of thin film samples showed that tetragonal phase of ZrO_2 and amorphous phase of SiO_2 were observed. The narrowing of the diffraction peak width indicates the better crystallinity of the films at higher content of zirconia. The luminescence spectra of thin films showed that there was an increase in the emission intensity which results in the enhancement of the green and red emission from the samples. The observed emission spectra exhibit three strong emission bands centered at 578 nm, 655 nm and 678 nm which correspond to the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition respectively. The addition of ZrO_2 into the silica glass matrix facilitates the Er^{3+} ions to disperse homogeneously within the matrix and thus promotes intense luminescence intensity. For nanofibres samples, PVA solution was added into the $(100-x)\text{SiO}_2-(x)\text{ZrO}_2$ doped 0.58 mol% Er^{3+} solution in order to achieve desired viscosity for electrospinning process. Based on FESEM images, the images of $(100-x)\text{SiO}_2-(x)\text{ZrO}_2$ doped 0.58 mol% Er^{3+} /PVA nanofibres samples showed the electrospun nanofibres consisted of smooth and uniform surfaces with random orientation. The nanofibres images after the calcinations process at 600°C showed the surface morphology of nanofibres is well preserved and exhibits shrinkages with average diameters reduced by about 25%. Finally, the luminescences properties of nanofibres as compared to thin film have showed that nanofibres sample demonstrate higher intensity of emission and shifting the erbium emission to the lower wavelength.

ACKNOWLEDGEMENT

In the name of Allah The Most Beneficent and The Most Merciful for giving me the strength in completing this work and thesis. It is most humbleness and gratitude that this work is finally completed with His Blessing.

In particular, I would like to record my sincere appreciation to my supervisor, Prof. Dr. Mohd Kamil Abd Rahman for his guidance, valuable advice, attention and valuable suggestions in assisting me to complete my master project. My special thanks and appreciation also goes to my senior, Nurul Iznie Razaki for her guidance, help and teaching me the ways of preparing sol gel method and thin films fabrications. My acknowledgement also goes to all the lab assistant of Faculty of Applied Science for their co-operations. I am very grateful for the excellent laboratory facilities provided by faculty during my study.

No words can be used to express my deepest gratitude to my parents and family for giving me moral support, encouragement and advice to complete my MSc. Lastly, I would like to thanks my colleagues for their opinions during the experiment, monitoring and discussion session. Without their continued support an interest, this thesis would not have materialized. To those who indirectly contributed in this research, your kindness means a lot to me. I hope my thesis can be used as a guideline in the future.

Thank you very much.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF SYMBOLS	xiii
LIST OF ABBREVIATIONS	xiv
CHAPTER ONE: INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	4
1.3 Objectives of The Research	4
1.4 Scope of Research	5
1.5 Significance of Study	5
1.6 Content of Thesis	6
CHAPTER TWO: LITERATURE REVIEW	7
2.1 Determination of Erbium (Er ³⁺)	7
2.1.1 Ion Clustering at Higher Er ³⁺ in Silica (SiO ₂)	10
2.1.2 Higher Doping of Er ³⁺	10
2.2 Host Material	12
2.2.1 Silica (SiO ₂)	12
2.2.2 Zirconia (ZrO ₂)	13
2.2.3 SiO ₂ -ZrO ₂ Doped Er ³⁺	14
2.2.4 Glass Ceramic (Zr, Hf, Ti)	16
2.2.5 Alumina (Al ₂ O ₃)	17
2.2.6 Phosphorus Pentoxide (P ₂ O ₅)	18

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Erbium is a well known rare earth element that has been classified into the group of the lanthanides. The symbol of Er contains atomic number of 68 with electronic configuration of $[\text{Xe}] 4f^{12} 6s^2$, where $[\text{Xe}]$ represents the close shell electronic configuration of xenon. Erbium normally assumes as the trivalent charge state (Er^{3+}) with an electronic configuration of $[\text{Xe}] 4f^{11}$ in most materials. The Er^{3+} appears as pink-colored salt. Er^{3+} emission is frequently used for optical doping to modify the electronic properties of the material. Most of rare-earth ions such as Er^{3+} ions are present luminescence. Luminescence is defined as the emission from an excited electronic state [1]. When the ion is excited, it absorbs energy which causes an electron to jump from the ground level to the excited level. Then, the electron will fall back to the ground level and releasing the excess energy in the form of photon. Recently, Er^{3+} ions are well known material for optical signal amplification at C-band (1550 nm) region [2]. It is known that erbium amplification at 1550nm coincides with low loss region of silica fibers [3].

Silicon dioxide (SiO_2) is also known as silica which comprised of silicon and oxide. Naturally, silica is found in two different forms that are amorphous and crystalline. Silica network former (SiO_4)²⁻ is consist of silicon atom at the centre of a tetrahedron with an oxygen atom bonded to each corner. The strong electron bond which exists between the silicon (Si) and oxygen (O) atoms offers the silica glass its impressive mechanical strength and thermal properties. SiO_2 is one of the most significant materials in optics industry. It is widely used for the optical fiber and waveguides [4]. Previously, SiO_2 glass has been efficiently used as the basic host of Er^{3+} ions due to the coincidence between the standard telecommunication wavelengths at 1550 nm and lowest loss region in the absorption spectra of silica glass. In order to comply with integrated optics (IC) technology, large concentrations of Er^{3+} ions must be homogeneously built-in to the glass matrix to achieve high optical amplification gain. Unfortunately, above certain doping levels, rare earth ions incline to form