

**UNIVERSITI TEKNOLOGI MARA**

**THULIUM DOPED (SILICA-  
ALUMINA) HYBRID NANOFIBER  
AND THIN FILM MULTILAYERED  
STRUCTURE**

**NURUL IZNIE BINTI RAZAKI**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Doctor of Philosophy**  
(Science)

**Faculty of Applied Sciences**

**December 2019**

## ABSTRACT

High intensity of rare earth ion emission in silica ( $\text{SiO}_2$ ) is highly desirable for photonics applications such as laser, display, etc. Incorporation of alumina ( $\text{Al}_2\text{O}_3$ ) in  $\text{SiO}_2$  would reduce ion clustering and phonon energy of the glass, therefore enhance the rare earth ion emission intensity. However, previous study has shown that the rare earth ions clustering is still identifiable that it would affect the ion emission. Incorporation of the rare earth ions in nanosized structure is beneficial for unique and enhanced emission intensity. Thulium ( $\text{Tm}^{3+}$ ) doped  $90\text{SiO}_2\text{-}10\text{Al}_2\text{O}_3$  (mol%) nanofibers were successfully fabricated by the sol-gel/electrospinning techniques. The nanofibers retain the fibrous structure after thermal treatment at  $950^\circ\text{C}$ .  $\text{Tm}^{3+}$  doped  $\text{SiO}_2\text{-Al}_2\text{O}_3$  nanofiber and thin film multi-layered structure demonstrates broad spectral width with notable high emission intensity. This multilayer structure comprised of thin film sandwiched between two nanofiber layers. The emission spectrum exhibited more than five-fold enhancement at 680 nm wavelength and about 51 nm spectral bandwidth, as compared to the emission from a thin film layer. The emission peaked at shorter wavelength by about 30 nm from the spectral peak of thin film. The manifestation of the nanostructured layers, which alters the energy levels of  $\text{Tm}^{3+}$  due to confinement of the ions in low dimensional structure combined with the effect from thin film, resulted in the spectral broadening and increased of emission intensity. The order of depositing nanofiber and thin film layers affects the luminescence intensity and peak spectrum wavelength. Thus, tailoring the order in which these layers are to be deposited allows a particular emission characteristic to be achieved.

## **ACKNOWLEDGEMENT**

In the name of Allah The Most Beneficent and The Most Merciful for giving me the strength in completing this work and thesis. In the first place, I sincerely would like to thank to my supervisor, Prof. Dr. Mohd Kamil Abd. Rahman for his patience supervising, valuable advice, attention and guidance at all stages in my research work. With his guidance and support, I was able to complete this study.

I would like to thank Ministry of Higher Education, Malaysia for providing scholarship for my doctoral study. Furthermore, I am grateful for the excellent laboratory facilities provided by Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam during my study.

Most importantly, thanks to my beloved parent, husband and daughter for their love, trust and support throughout my study. I appreciate the support of my colleagues from UiTM Photonics Research Group for whom I had the pleasure of knowing and working with. Not to forget, thanks to my friends who always support and motivate me during my study. Alhamdulillah.

# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	<b>ii</b>
<b>AUTHOR'S DECLARATION</b>	<b>iii</b>
<b>ABSTRACT</b>	<b>iv</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>TABLE OF CONTENTS</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>x</b>
<b>LIST OF FIGURES</b>	<b>xi</b>
<b>LIST OF PLATES</b>	<b>xviii</b>
<b>LIST OF SYMBOLS</b>	<b>xix</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xx</b>
<b>LIST OF NOMENCLATURES</b>	<b>xxi</b>
<b>CHAPTER ONE: INTRODUCTION</b>	<b>1</b>
1.1 Research Background	1
1.2 Problem Statement	3
1.3 Objectives	4
1.4 Scope and Limitation of the Research	4
1.5 Significance of Study	6
1.6 Brief Content of the Thesis	6
<b>CHAPTER TWO: LITERATURE REVIEW</b>	<b>8</b>
2.1 Introduction To Glass, Silica, Alumina, Silica-Alumina Glass System and Poly (vinyl) Alcohol	8
2.1.1 Glass	8
2.1.1.1 <i>Silica Glass</i>	9
2.1.2 Alumina (Al <sub>2</sub> O <sub>3</sub> )	12
2.1.3 SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> Glass Ceramic System	14
2.1.4 Poly (vinyl) Alcohol	15
2.2 Sol-Gel Technique for Silica Glass Formation	17

# CHAPTER ONE

## INTRODUCTION

### 1.1 Research Background

Various rare earth ions are of interest due to their potential in numerous range of applications including laser technology (Vienne et al., 1998; Moncorgé, Merkle and Zandi, 1999; Managaki et al., 2006; Bourhis et al., 2015; Gao, et al., 2015), display device (Leskelä and Niinistö, 1992; Ballato, Lewis and Holloway, 1999; Suyver et al., 2006), optical amplifier (Feuchter et al., 1992; Mukherjee, 2000; Minh et al., 2002; Son et al., 2014), optical sensor (Potter and Sinclair, 1998), etc. It is known that the rare earth elements provide a large number of available absorption and emission bands that are useful for many optical and photonics applications. For example, in visible (VIS) region, europium ( $\text{Eu}^{3+}$ ) ion emits red (Nogami and Abe, 1996; Jia, Shao and Han, 2013; Ran et al., 2018) terbium ( $\text{Tb}^{3+}$ ) ion emits green, (Armellini et al., 1999; Xia et al., 2015) and thulium ( $\text{Tm}^{3+}$ ) ion emits blue and weak red, (Bonar et al., 1997; Otto, Brewer and Silversmith, 2000) colour. These rare earth ions materials are beneficial for laser and lighting applications. Meanwhile, in the near infra-red region,  $\text{Er}^{3+}$  (Benatsou et al., 1997; Filho et al., 2015; Aboud, 2016) and  $\text{Tm}^{3+}$  (Gao et al., 2015; Wang et al., 2015) ions are widely used for signal amplification in an optical amplifier.

Silica ( $\text{SiO}_2$ ) glass has been widely used as the rare earth host due to its outstanding properties such as high transparency over a wide range of wavelength, high mechanical strength, strong thermal resistance, inexpensive, etc. (Mukherjee, 1980; Qiao et al., 2007; Wu, et al., 2012; Wang et al., 2015). In photonics application, high photoluminescence intensity of the rare earth ion is desired for the efficiency of the optical device. Therefore, a high concentration of the rare earth ions is needed as a dopant in  $\text{SiO}_2$  glass. However, the presence of a high amount of the rare earth leads to the ions clustering which is due to their low solubility in  $\text{SiO}_2$  host matrix (Wang et al., 2015). This is due to the rigid structure of  $\text{SiO}_2$  glass and the insufficient number of non-bridging oxygen atoms in  $\text{SiO}_2$  glass that would cause the rare earth ions to cluster among each other (Auzel and Goldner, 2001; Monteil, et al., 2004). As the