

**UNIVERSITI TEKNOLOGI MARA**

**EFFECTS OF Ce<sup>4+</sup> AND Cd<sup>2+</sup>  
SUBSTITUTIONS ON  
SUPERCONDUCTING  
FLUCTUATION BEHAVIOR,  
ULTRASONIC VELOCITY AND  
ELASTIC PROPERTIES OF Fe-  
DOPED (Tl, Bi)-1212 HIGH  
TEMPERATURE  
SUPERCONDUCTORS**

**SHABANI BINTI ISMAIL**

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

**Faculty of Applied Sciences**

**July 2015**

## ABSTRACTS

In this study, two series of superconductor compounds with starting composition  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-x}\text{Ce}_x\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.20$ ) and  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{1.8}\text{Yb}_{0.2}\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.4$ ) ceramics were prepared using the conventional solid-state synthesis method to elucidate their physical properties. For Ce-substituted of  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-x}\text{Ce}_x\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.20$ ) samples, the zero critical temperature,  $T_{c\text{ zero}}$  increased from 65.4 K ( $x = 0.05$ ) to 71.0 K ( $x = 0.10$ ), but slightly decreased for  $x > 0.10$  indicating the optimum value of average copper valence was achieved at  $x = 0.10$ . Excess conductivity analysis using the Aslamazov Larkin, AL and Lawrence–Doniach, LD models revealed two dimensional, 2D to three-dimensional, 3D transition of superconducting fluctuation behavior, SFB with the highest transition temperature,  $T_{2D-3D}$  at  $x = 0.10$ . FTIR analysis in conjunction with XRD results showed softening of  $\text{FeO}_2/\text{CuO}_2$  planar oxygen mode which is suggested to be related to possible increase of interplane coupling,  $J$  and this is supported by computed results based on the LD model. The enhanced  $J$  increases superconducting coherence length along  $c$ -axis,  $\xi_c(0)$ , and hence lowers anisotropy,  $\gamma$  resulting in enhanced superconducting properties. For  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{1.8}\text{Yb}_{0.2}\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.4$ ) ceramics, substitution of Cd caused  $T_{c\text{ zero}}$  increasing from 40.0 K ( $x = 0$ ) to 76.4 K ( $x = 0.3$ ) before decreasing to 74.8 K ( $x = 0.4$ ) with increasing  $\text{Cd}^{2+}$  contents. FTIR analysis in conjunction with XRD results indicates improved  $J$  that is evidenced in the form of decreased  $c$ -axis length and softening of the apical oxygen mode with Cd concentration. Excess conductivity analyses showed cross-over between 2D to 3D SFB transition for all the samples ( $x = 0.1-0.4$ ) with the highest  $T_{2D-3D}$  was observed at  $x = 0.3$ . Similar calculation revealed longest value of  $\xi_c(0)$  and the highest  $J$  at  $x = 0.3$ . Ultrasonic velocity measurements was performed on longitudinal and shear velocities at 9 MHz in temperature ranges of 80–280 K and 80–220 K, respectively, for  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{1.8}\text{Yb}_{0.2}\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.4$ ) and  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-x}\text{Ce}_x\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.2$ ) ceramics to study the influence of Cd and Ce substitutions on elastic properties and elastic anomaly. For the former series, ultrasonic velocity measurements at 80 K showed a non-linear increase in both absolute longitudinal and shear velocities as well as elastic moduli with Cd substitution with the largest increase observed for the  $x = 0.3$  sample. Temperature dependant longitudinal modulus showed elastic anomaly characterized by a step-like slope change at around 230 K for  $x = 0$  &  $x = 0.3$  and around 250 K for  $x = 0.4$  with the  $x = 0.3$  sample showing the sharpest slope change. For  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-x}\text{Ce}_x\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  series, Ce was observed to influence elastic moduli at 80 K which showed the largest value obtained at  $x = 0.10$ . A longitudinal velocity anomaly was observed at around 260 K for the unsubstituted sample ( $x = 0$ ). Ce substitution caused the temperature of the elastic anomaly to shift to 250 K ( $x = 0.1$ ) and 262 K ( $x = 0.2$ ). The existence of the step-like elastic anomaly was suggested to be due to oxygen ordering taking place in Tl-O planes. The analysis of the elastic behavior in the vicinity of the elastic anomalies using Landau free-energy model for both  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{1.8}\text{Yb}_{0.2}\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.4$ ) and  $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-x}\text{Ce}_x\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_{1.99}\text{Fe}_{0.01}\text{O}_{7-\delta}$  ( $x = 0-0.2$ ) series suggests that the anomaly is due to a phase transition which involves oxygen ordering.

## ACKNOWLEDGEMENT

Assalamualaikum w.b.t.

All praise to Allah S. W. T., the most Beneficent and the Most Merciful, for granting the completion of this thesis.

My first and foremost gratitude to my helpful supervisor, Prof. Dr. Ahmad Kamal Hayati Bin Yahya, whose learned advice, invaluable support and guidance. His suggestion, criticism and willingness to motivate me contributed tremendously towards the completion of this project. I would also like to express my sincere thanks to my co-supervisor Dr Abdel-Baset M. A. Ibrahim for helping and teaching me how to operate the Matlab software as well as sharing his knowledge and ideas to the success of the project and hence the thesis.

Then, sincere thanks to the following people for the wonderful helpful and technical support they gave me: Puan Juliana Karim (X-Ray Diffraction), Mr. Hayub (Scanning Electron Microscope) and the Faculty of Applied Science's laboratory assistant at the Blok G who had helped me in numerous ways in accomplishing this research. Not forgetting also to Assoc. Prof. Dr. Nawazish Ali Khan from Quaid-i-Azam University, Pakistan for his helped me in the FTIR measurements. To all of them, I accord my sincere gratitude.

Further thanks and appreciation should also go to my friends, Norazila, Suhadir, Nurul Huda, Azliza, Mohd Muzammir, Muliana and others for their friendship, suggestions and spiritual support throughout my research work

The financial support provided by the Universiti Teknologi MARA (UiTM) through fellowship are also gratefully acknowledged and appreciated here. Besides, I would also like to thank the management of the Faculty of Applied Sciences and Universiti Teknologi MARA (UiTM) for providing a good study environment and adequate research facilities to complete this project. .

Last but not least, my greatest thanks and million hands of gratitude to my beloved husband, Mohd Azhar Bin Zainul Abidin for his patience and cheerful support during the completion of this thesis. A big thank you also goes to my parents and all my family members for this silent prayers, love, support and courage that had been shared with me.

Thank you.

## TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	ii
<b>AUTHOR'S DECLARATION</b>	iii
<b>ABSTRACT</b>	iv
<b>ACKNOWLEDGEMENT</b>	v
<b>TABLE OF CONTENTS</b>	vi
<b>LIST OF TABLES</b>	x
<b>LIST OF FIGURES</b>	xii
<b>LIST OF SYMBOLS</b>	xx
<b>CHAPTER ONE: INTRODUCTION</b>	
1.1 Background of Research	1-6
1.2 Problem Statement	6-8
1.3 Objectives of Study	8-9
1.4 Significance of the Study	9-10
<b>CHAPTER TWO: LITERATURE REVIEW</b>	
2.1 Introduction	11
2.2 A Brief History of Superconductivity	12-15
2.3 Basic Properties of Superconductors	15
2.3.1 Zero Resistance ( $R = 0$ )	16-17
2.3.2 The perfect diamagnetism ( $B = 0$ )	17-18
2.4 Types of Superconductors	19
2.4.1 Type I	19-21
2.4.2 Type II	21-22
2.5 Theory of Superconductivity	22-24
2.6 Characteristic Phenomenological Parameters	
2.6.1 The Magnetic Penetration Depth	25-26

# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND OF RESEARCH

Superconductivity is a relatively modern phenomenon that was discovered in the past century. A superconductor is a metal compound that when cooled to a very low temperature (below its critical temperature or  $T_c$ ), has no electrical resistance and expels all external magnetic fields (Ketterson & Song, 1999). Superconductivity was first discovered by Heike Kamerlingh Onnes in 1911 when he cooled a sample of mercury to liquid helium temperatures. In 1986, Alex Muller and George Bednorz discovered copper oxide compounds which the highest known superconducting transition temperature above 30 K (Fisher et al., 1991). After this discovered, the search for high temperature superconductors (HTSC) was resumed. The number of scientists working in the field of superconductivity increased and various type of HTSC materials had been studied such as Y-Ba-Cu-O (or other rare earths based superconductor) (Wu et al., 1987; Siegrist et al., 1987), Bi-based (Xu et al., 1990; Tallor et al., 1998), Tl-based (Sheng, & Hermann, 1998; Parkin et al., 1988; Kaneko et al., 1992) and Hg-based (Meng et al., 1993; Schilling et al., 1993; Putilin et al., 1993) superconductor with  $T_c$  of up to 95 K, 110 K, 127 K, and 134 K (Park & Synder, 1995).

Thallium based superconductors are one of the largest family in HTSC as its highest  $T_c$  is higher than the more widely studied YBCO superconductor which were first discovered by Sheng and Hermann in 1988. The thallium-based family with the chemical formula  $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$  (Parkin et al., 1988) which have single Tl-O layer that is insulating but acts as charge reservoir layer to supply carriers to  $CuO_2$  planes.  $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$  can exists in three different phases which are the Tl1201 ( $n = 1$ ), Tl1212 ( $n = 2$ ), and Tl1223 ( $n = 3$ ) phases that exhibit increase in  $T_c$  from 40 K ( $n = 1$ ) to 110 K ( $n = 3$ ) with increase in number of Cu-O planes per unit cell. Replacement of Ba by Sr in Tl1212 was reported to display superconductivity below  $T_c$  of around 70–80 K (Martin et al., 1989).