SUPERVISORS' DECLARATION

I hereby declare that I have checked the thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Honor) Material Technology.

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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MICROSTRUCTURAL AND ELECTRICAL PROPERTIES OF RARE EARTH IONIC DOPED CCTO CERAMICS

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DEDICATION

Special dedication of this grateful feeling to my…

Beloved father and mother;

Mr. Syed Abu Bakar Bin Syed Makah and Mrs. Halimah Binti Ahmad

For all of their love, supports and encouragement.

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In the name of Allah the Most Gracious, the Most Merciful.

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ABSTRACT

Calcium Copper Titanate (CCTO) is one of ceramics that is noteworthy for its extremely large dielectric constant in application of ceramics. In order to improve the properties and application of calcium copper titanate, the doping of rare earth which is lanthanum and ytterbium in calcium copper titanate ceramics are study. The synthesis of lanthanum and ytterbium doped calcium copper titanate are done by investigating on the microstructure of the calcium copper titanate ceramics itself. Then, the electrical properties of the doping lanthanum and ytterbium to calcium copper titanate ceramics also been studied and investigated. Lanthanum and ytterbium doped calcium copper titanate with $x = 0.005$ for each of them. The method used for the preparation of all samples is via conventional solid state reaction method. The powder undergoes calcined at temperature of 700 °C for about 8 hours and process into pellet. After that the pellet is then been sintered at temperature 1000°C for another 8 hours. The crystal structure is investigated. For the X-ray diffraction patterns, lanthanum and ytterbium ions has entered the unit cell and substituted the Ca^{2+} ions on the A site of cubic structure. The lattice parameter is decrease as decreasing ionic radius of rare earth elements. For FESEM micrograph, the grain size is decreasing as doping with lanthanum ions but increasing as doped with ytterbium ions. The average grain size of pure CCTO is 1.494 μm, 1.024 μm for La doped CCTO and 1.328 μm for Yb doped CCTO. The addition of lanthanum to the CCTO ceramics lead to drop in value of dielectric permittivity of CCTO ceramics. However, dielectric permittivity is increase once ytterbium is added to CCTO ceramics. The maximum dielectric permittivity of pure CCTO, La doped CCTO and Yb doped CCTO is 5.50×10^7, 4.18×10^7 and 2.43×10^7 at frequency of 1.00×10^3 Hz. Then, for the dielectric loss of CCTO ceramics is increase as doping with rare earth element. The dielectric loss of pure CCTO, La doped CCTO and Yb doped CCTO is 9.749×10^{-3},1.830×10^{-3} and 1.477×10^{-3}.

ABSTRAK

Kalsium kuprum titanat adalah salah satu seramik yang mempunyai tarikan terhadap ciri dielektrik yang sangat tinggi dalam aplikasi seramik. Dalam usaha untuk meningkatkan ciri-ciri dan aplikasi kalsium kuprum titanat, doping dengan nadir bumi seperti lanthanum dan ytterbium telah dikaji. Sintesis doping lantanum dan ytterbium dalam kalsium kuprum titanat telah dilakukan dengan menkaji mikrostruktur seramik itu. Seterusnya, sifat elektrik doping lantanum dan ytterbium dalam kalsium kuprum titanat juga dikaji. Penambahan komposisi dopan lantanum dan ytterbium dalam kalsium kuprum titanat dengan $x = 0.005$. Kaedah yang digunakan untuk menyediakan kesemua sampel adalah kaedah tindak balas keadaan pepejal yang konvensional. Serbuk tersebut perlu melalui kalsin pada suhu 700 °C selama 8 jam dan diproses membentuk pelet. Selepas itu, pelet itu disinter pada suhu 1000°C untuk 8 jam lagi. Kajian telah dijalankan keatas struktur kristal. Untuk kajian corak pembelauan X-ray, didapati ion lantanum dan ytterbium memasuki sel unit dan menggantikan ion kalsium di sudut A struktur kubik. Kekisi parameter berkurang seiring pengurangan radius ionik elemen-elemen nadir bumi. Untuk kajian FESEM mikrograf, saiz bijirin berkurang apabila doping dengan ion lantanum tetapi meningkat apabila didoping dengan ion ytterbium. Purata saiz bijirin untuk CCTO asli, La doping CCTO dan Yb doping CCTO adalah 1.494 µm, 1.024 µm dan1.328 µm. penambahan lantanum ke atas seramik CCTO membawa kepada penurunan permitiviti dielektrik. Walau bagaimanapon permitiviti dielektrik meningkat apabila ytterbium didoping ke atas seramik CCTO. maksimum permitiviti dielektrik untuk CCTO asli, La doping CCTO dan Yb doping CCTO adalah 5.50×10^7, 4.18×10^7 and 2.43×10^7 pada frekuensi 1.00×10^3 Hz. Kehilangan dielektrik untuk CCTO asli, La doping CCTO dan Yb doping CCTO adalah 9.749×10^{-3},1.830×10^{-3} dan 1.477×10^{-3}.

TABLE OF CONTENT

DECLARATION	
TITLE PAGE	
ACKNOWLEDGEMENTS	**ii**
ABSTRAK	**iii**
ABSTRACT	**iv**
TABLE OF CONTENT	**v**
LIST OF TABLES	**viii**
LIST OF FIGURES	**ix**
LIST OF SYMBOLS	**x**
LIST OF ABBREVIATIONS	**xi**
CHAPTER 1 INTRODUCTION	**1**
1.1 Background of The Problem	1
1.2 Problem Statement	2
1.3 Objectives of Study	3
1.4 Scoped of Study	3
CHAPTER 2 LITERATURE REVIEW	**5**
2.1 History of CCTO Ceramics	5
2.2 Doping RE To CCTO	6

2.3 Elements Doped CCTO at Ca^{2+} Site 8

2.4 Microstructural Analysis of RE Doped CCTO Ceramics 9

2.5 Dielectric Properties of Doped RE To CCTO Ceramics 10

CHAPTER 3 MATERIALS AND METHOD 12

3.1 Introduction 12

3.2 Chemicals and Solvents 14

3.3 Equipment 15

3.4 Sample Preparation 16

3.4.1 Grinding Method 16

3.4.2 Pelletizing Method 17

3.4.3 Sintering Method 18

3.5 Sample Characterizations 19

3.5.1 X-ray diffraction (XRD) 19

3.5.2 Field Emission Scanning Electron Microscope (FESEM) 20

3.5.2 Potentiostat 21

3.6 Flow Chart 22

CHAPTER 4 RESULTS AND DISCUSSION 23

4.1 Synthesis and Characterization of CCTO Ceramics 23

4.1.1 X-ray Diffraction Analysis 23

4.1.2 Field Emission Scanning Electron Microscopy (FESEM) 26

4.2 Electrical Analysis of Pure CCTO, La-doped CCTO & Yb-doped CCTO Ceramics 28

CHAPTER 5 CONCLUSION AND RECOMMENDATION **33**

5.1 Conclusion 33

5.2 Recommendations 34

REFERENCES **35**

APPENDIX A SAMPLE APPENDIX 1 **37**

LIST OF TABLES

Table 2.0	Doping of rare earth to CCTO	7
Table 2.1	Element that is doped at Ca^{2+} site	8
Table 2.2	Microstructural Analysis of RE doped CCTO Ceramics	9
Table 2.3	Dielectric properties of rare earth ions doping of CCTO Ceramics	10
Table 3.1	List of chemicals and solvents used in the study	14
Table 3.2	List of equipment used in the research	15
Table 4.0	Value of lattice parameter, ionic radius and mean grain size of pure CCTO, La-CCTO and Yb-CCTO at phase (2 2 0)	24
Table 4.1	Value of lattice parameter and grain size of pure CCTO, La-CCTO and Yb-CCTO	27
Table 4.2	Value of dielectric constant of pure CCTO, La doped CCTO and Yb doped CCTO	30
Table 4.3	Value of dielectric loss for pure CCTO, La-CCTO and Yb-CCTO at frequency of 1.00×10^2	32

LIST OF FIGURES

Figure 3.0	An image of mortar and pestle	16
Figure 3.1	An image of uniaxial pressing machine	17
Figure 3.2	An image of Lindberg/Blue M^{TM} Box Furnaces	18
Figure 3.3	An image of Rigaku Miniflex X-ray diffractometer	19
Figure 3.4	An image of Field Emission Scanning Electron Microscopy from JSM-7800 brand	20
Figure 3.5	An image of potentiostat from AUTOLAB brand	21
Figure 3.6	Flowchart procedure of synthesis pure CCTO, La doped CCTO and Yb doped CCTO	22
Figure 4.0	XRD pattern of pure CCTO, La-CCTO and Yb-CCTO	23
Figure 4.1	XRD shifting pattern of pure CCTO, La-CCTO and Yb-CCTO	25
Figure 4.2	The image of grain size for pure CCTO, La-CCTO and Yb-CCTO at magnification of x= 5k	26
Figure 4.3	Frequency dependence of dielectric permittivity value of pure CCTO, La-CCTO and Yb-CCTO	28
Figure 4.4	Frequency dependence of dielectric loss value of pure CCTO, La-CCTO and Yb-CCTO	31

LIST OF SYMBOLS

~	Approximation
%	Percent
ε_o	dielectric permittivity
ε''	dielectric loss
2θ	Bragg angle
°C	degree celcius
Å	angstrom (10^{-10})
Z_i	imaginary impedance
Zr	real impedance
g	grams
h	hour
t	time

LIST OF ABBREVIATIONS

CCTO	calcium copper titanate
FESEM	field emission scanning electron microscopy
XRD	X-ray diffraction
RE	rare earth
La	lanthanum
Nd	neodymium
Eu	europium
Gd	gadolinium
Er	erbium
Yb	ytterbium
Pr	praseodymium
Y^{3+}	yttrium
IBLC	internal barrier layer capacitor

CHAPTER 1

INTRODUCTION

1.0 Background of problem

Ceramics is known as an inorganic, non-metallic solid material that consist of metal, non-metallic and metalloid metal atoms. The atoms are held in ionic and covalent bonds. Therefore, most of the ceramics materials have good thermal and electrical insulators. Some of the basic properties of ceramics are high melting temperature, high conductivity, high moduli of elasticity and chemical resistance. In past years, the earliest ceramics are made from clay, either pure clay or mixed with other element like silica, hardened and sintered in fire. Currently, there are many improvement in the ceramics field till it is included in domestic, industrial and also building products. For instance, Alumina, Aluminium Nitride, Zirconia, Silicon Nitride, Silicon Carbide and also semiconductor which also a new advanced ceramic materials.

Nowadays, Calcium copper titanate ($CaCu_3Ti_4O_{12}$) have been discovered as one of best ceramics for electronic application. $CaCu_3Ti_4O_{12}$ is CCTO type of ceramics that is come with very good quality as it having good electrical properties. The advantages or uniqueness of this CCTO ceramics is that it have an extraordinary high dielectric permittivity of $\sim 10^5$. Dielectric permittivity is referred as a quantity for measuring the ability of substance to store electrical energy in an electric field. Besides that, it also show a good temperature stability from 100K to 600K and does not undergo any structural phase transitions from 20 K- 600K. All those properties has make CCTO become very important material for many electronic application such as capacitor –based applications, microwave communication devices, switching and energy storage devices (Liu et al. 2015).

But, the fact that giant dielectric properties of CCTO is accompanied with strong increase in dielectric loss which then also cause an obstruction to the applications of CCTO (Liu et al. 2015). Dielectric loss is defined as loss of electromagnetic energy propagating inside a dielectric. Due to this issue many researcher are continuously on proposing their own theoretical models as a way to further explain the origin of dielectric permittivity with high dielectric loss as well as to maintain the good properties of the CCTO ceramics itself. Many elements from the periodic table have been utilized by the researchers in order to investigate on their effect as a dopant to the CCTO ceramics properties. However, there is limited research on the use of rare earth ions group as dopant for the CCTO.

Therefore, one theoretical model is proposed which is by applying various rare earth ions with different ionic radius as dopant to CCTO ceramics. The proposed of this research is to further investigate on the effect of different ionic radius of RE ion to the microstructural characteristic and electrical properties of CCTO. Besides that, this research will lead to the approval of the ability of RE ions group as an element that able to enhance the properties of CCTO ceramics. Therefore, two element of rare earth ion group that has been chose for this research is La^{3+} and Yb^{3+}.

1.2 Problem statement

Theoretically, many researchers have proposed their model on doping CCTO ceramics with lot of elements include rare earth ion group (RE^{3+}). However, there is no abundance proof that show the effect of RE doping to the microstructural characteristic and electrical properties of CCTO ceramics. Therefore, the research of applying different ionic radius of RE doped with CCTO ceramics is proposed. The two RE ions group that is chose for this research is La^{3+} and Yb^{3+}.

1.3 Objectives of study

Objectives of this research are:

1. To synthesis the rare earth, La^{3+} and Yb^{3+} doped $CaCu_3Ti_4O_{12}$ ceramics by solid state reaction.
2. To investigate the influence of rare earth dopant (La^{3+} and Yb^{3+}) to microstructural characteristic of $CaCu_3Ti_4O_{12}$ ceramics.
3. To study the effect of different ionic radius of rare earth dopant (La^{3+} and Yb^{3+}) to electrical properties of $CaCu_3Ti_4O_{12}$ ceramics.

1.4 Scope of the study

This proposed research would be involving the test on Calcium Copper Titanate ($CaCu_3Ti_4O_{12}$) which is a type of CCTO ceramics that will be doped with two rare earth ion group, Lanthanum Oxide (La_2O_3) and Ytterbium Oxide (Yb_2O_3). Basically the method used in this model is solid state reaction method which is involved the conventional sintering route, using analytical-grade (≥99.5%) powders of $CaCO_3$, CuO and TiO_2 as starting materials (Liu et al. 2015). The composition of $CaCO_3$, CuO and TiO_2 is weight according to the stoichiometric ratio of 1:3:4 and mix with different concentration of La^{3+} and Yb^{3+} ions.

Three different samples prepared for this research, first is pure CCTO, second CCTO doped with 0.005 wt% La^{3+} and third is CCTO doped with 0.005 wt% Yb^{3+}. The rare earth ion is doped at very small amount as way to avoid the formation of secondary phase. The second phase may form due to large disparity between ionic radius of Re^{3+} and Ca^{2+} which causes the excess of La^{3+} and Yb^{3+} substitute at the Ca site of CCTO lattice. Furthermore, not all La^{3+} and Yb^{3+} will easily enter the lattice of CCTO ceramics as some of them may remain concentrated at the grain boundary.

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