EFFECTS OF SINTERING TEMPERATURE ON MORPHOLOGY AND DIELECTRIC PROPERTIES OF $SrTiO_3$-DOPED $CaCu_3Ti_4O_{12}$ PREPARED VIA MECHANICAL ALLOYING

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ITMA 2018 22

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By

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

December 2018

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

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December 2018

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Perovskite materials are well known for their ability to produce high dielectric constant which had led to many important industrial applications in microelectronics and memory devices. In this research, the relationship between morphology and dielectric properties of perovskite Strontium Titanate, ST and the perovskite-related material Calcium Copper Titanate, CCTO were studied. Most of the works done on CCTO-ST system basically cover the composition of CCTO-ST towards their electrical properties, effect of doping and their dielectric and microstructure relationship at higher sintering temperatures. However, not much work was done on tracking the evolution of CCTO-ST at low sintering temperature until they evolve to their final sintering temperature. Hence, in this thesis, research findings on the parallel evolution of such morphological properties and dielectric properties were reported and elucidate their relationship. CCTO, ST and CCTO doped with ST were prepared via mechanical alloying using High Energy Ball Milling in a hardened steel vial for 10, 12 and 2 hours respectively. The pellet samples were sintered from 500 °C to final temperature at 100 °C increment. The phase and crystal structure formation of the synthesized materials were confirmed by X-ray diffraction (XRD) while the evolution of microstructure properties was studied using Field Emission Scanning Electron Microscopy, FeSEM. The as-milled ceramic confirmed the existence of CCTO peak for the CCTO and CCTO-ST samples. After the sintering process, the highly crystalline phase of ST, CCTO and CCTO-ST was form at 1000 °C, 1000 °C and 800 °C respectively. FeSEM revealed an improvement in grain growth as the sintering increased where the grain size increased from 126.5 nm to 559.6 nm (ST), 82 nm to 18467 nm (CCTO) and from 114.54 nm to 1658.02

nm (CCTO-ST). The relative densities also show an increment where it reaches 73.59%, 98.92% and 22.26% for CCTO, ST and CCTO-ST respectively at their final sintering temperature. The dielectric studies were carried out by using Impedance Analyzer in the frequency range 40 Hz to 1 MHz and varies from 30 °C to 200 °C. For ST samples, the dielectric constant showed interfacial polarization at low frequency and ε_r' value increases from 49.753 to 517.603 at 100 kHz as the sintering temperature arise. Meanwhile, tangent loss (tan δ) was found in the range of 0.069 to 0.02 at 100 kHz at room temperature. For CCTO, the permittivity studies showed two polarizations occur. The relaxation belonged to the interfacial polarization. At 100 kHz, the ε_r' varies from 72 to 5573 for CCTO samples sintered at 500 ^{o}C to 1100 ^{o}C. The frequency dependence of loss tangent, tan δ decreased to almost zero at higher frequencies for all sintering temperatures. The influence of ST on CCTO system does improved the microstructure and reduced the dielectric properties. The dielectric constant for CCTO-ST nanocomposite is lower than in CCTO ceramics which in the range of 139.956 at 100 kHz. However ST as a dopant also reduced tan δ to 0.03. CCTO-ST sintered at 1000 ˚C showed a prominent candidate for energy storage devices as it has the lowest tangent loss and moderate ε_r'.

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

KESAN SUHU KE ATAS SIFAT MORFOLOGI DAN SIFAT DIELEKTRIK $SrTiO_3$-DIDOPKAN KEPADA $CaCu_3Ti_4O_{12}$ DISEDIAKAN MELALUI KAEDAH PENGALOIAN MEKANIKAL

Oleh

MUTIA SUHAIBAH BINTI ABDULLAH

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Bahan perovskite terkenal kerana keupayaannya menghasilkan pemalar dielektrik tinggi yang telah menyebabkan banyak aplikasi perindustrian penting dalam mikroelektronik dan peranti memori. Dalam kajian ini, hubungan antara morfologi dan sifat dielektrik perovskite Strontium Titanat, ST dan bahan berkaitan perovskite Kalsium Kuprum Titanat, CCTO telah dikaji. Kebanyakan kajian yang dilakukan pada sistem CCTO-ST pada dasarnya meliputi komposisi CCTO-ST terhadap sifat elektrik mereka, kesan doping dan hubungan dielektrik dan mikrostruktur mereka pada suhu sintering yang lebih tinggi. Walau bagaimanapun, tidak banyak penyelidikan yang dilakukan untuk mengesan evolusi CCTO-ST pada suhu sintering yang rendah sehingga mereka berubah menjadi suhu sintering terakhir mereka. Oleh itu, dalam tesis ini, beberapa penemuan penyelidikan mengenai evolusi selari sifat morfologi dan sifat dielektrik tersebut dilaporkan dan menjelaskan hubungan mereka. Seramik ST, CCTO dan CCTO didopkan ST telah disediakan melalui kaedah pengaloian mekanikal menggunakan pengisaran bebola bertenaga tinggi di dalam botol keluli keras selama beberapa jam. Bagi mendapatkan siri suhu yang berubah, sampel disinterkan dari suhu 500 ke 1400 °C pada peningkatan 100 °C. Pembentukan struktur fasa dan kristal bahan-bahan yang disintesis telah disahkan oleh analisis pembelauan sinar-X (XRD) manakala evolusi sifat-sifat mikro telah dikaji menggunakan Mikroskopi Pengimbasan Elektron Pelepasan Medan, FeSEM. Seramik sesudah pengisaran mengesahkan adanya puncak CCTO untuk sampel CCTO dan CCTO-ST. Selepas proses pemanasan, fasa ST, CCTO dan CCTO-ST yang sangat kristal dibentuk pada 1000 °C, 1000 °C dan 800 °C. Pemerhatian oleh FeSEM menunjukkan peningkatan dalam pertumbuhan bijirin apabila sintering meningkat di mana saiz butiran meningkat dari 126.5 nm ke 559.6 nm (ST), 82 nm ke 18467 nm (CCTO) dan dari 114.54 nm ke

1658.02 nm. Ketumpatan relatif juga menunjukkan kenaikan di mana ia mencapai 73.59%, 98.92% dan 22.26% untuk CCTO, ST dan CCTO-ST masing-masing pada suhu sintering terakhir mereka. Kajian dielektrik dilakukan dengan menggunakan Impedance Analyzer dalam julat frekuensi 40 Hz hingga 1 MHz dan berbeza dari 30 °C hingga 200 °C. Bagi sampel ST, pemalar dielektrik menunjukkan polarisasi interfacial pada frekuensi rendah dan nilai ε_r 'meningkat daripada 49.753 ke 517.603 pada 100 kHz apabila suhu sintering meningkat. Sementara itu, kehilangan tangen didapati dalam julat 0.069 hingga 0.02 pada 100 kHz pada suhu bilik. Bagi CCTO, kajian ketelusan menunjukkan dua polarisasi berlaku. Kelonggaran itu tergolong dalam polarisasi antara muka. Pada 100 kHz, ε_r' berbeza dari 72 hingga 5573 untuk sampel CCTO yang disinter pada 500 °C hingga 1100 °C. Ketergantungan frekuensi kehilangan tangen, tan δ menurun kepada hampir nol pada frekuensi yang lebih tinggi untuk semua suhu sintering. Pengaruh sistem ST pada sistem CCTO memperbaiki struktur mikro dan mengurangkan sifat dielektrik. Pemalar dielektrik untuk nanocomposite CCTO-ST adalah lebih rendah daripada seramik CCTO iaitu 139.956 pada 100 kHz. Bagaimanapun ST sebagai dopan juga berkurangan tan δ kepada 0.03. CCTO-ST sintered pada 1000 °C menunjukkan calon yang terkenal untuk peranti storan tenaga kerana ia mempunyai kehilangan tangen terendah dan sederhana ε_r '.

ACKNOWLEDGEMENTS

Alhamdulillah, I praise and thank Allah for giving me the strength and patience to work through all these years.

To my supervisor, Associate Professor Dr Jumiah Hassan, thank you for introducing me to the field and for outlining this research, your help and guidance along the way. I also appreciate the control you gave me over this research and the freedom I had to pursue my own ideas.

I am deeply indebted my co-supervisor (late), Associate Professor Dr Mansor Hashim for his expert guidance and keen interest throughout the course of this study. Unfortunately, before completion of the thesis, he left us forever. I cherish his dedication in guiding me in my work despite of his ill health. I wish his soul rest in peace and solace in the heaven.

I would like to deeply thank the people who mean world to me, my parents, Hj Abdullah bin Daud and Hjh Fatilah Hasni Ab Latif. I cannot begin to say how much I appreciate their support and love. I would never be able to pay back the love and affection showered upon by my parents. I am especially grateful to my siblings for their endless patience and supporting me spiritually throughout my life.

I owe thanks to a very special person, my husband, Muhammad Aizat Noor Ismail for his continued support and understanding during my pursuit of Ph.D that made the completion of thesis possible. You were always around at times I thought that it is impossible to continue, you helped me to keep things in perspective.

Most importantly of all, I show extensive gratitude to my very best lab mates, Dayang Nur Fazliana Abdul Halim for always being there and bearing with me the good and bad times during my wonderful days of Ph.D. Without her willingness to share, the research would not have even been possible.

There are many more who deserve my gratitude, far too many to list here. Collective thanks to the Institute of Advanced Technology and Department of Physics, UPM for providing me with the requisite institutional facilities throughout my research tenure. I am equally thankful to Mrs. Sarinawani and Mr. Ali for their assistance with FeSEM measurements, Mr. Mohd Kadri Masaud and Dr. Ismayadi bin Ismail for the great contributions and helps, Mr. Mohd Anas Ahmad from USM and Mr. Nizam from UKM for making the facilities available during the research work.

My heartfelt thanks to my fellow labmates, Dr. Shamsul Ezzad, Dr. Rodziah Nazlan, Dr. Nor Hapishah Abdullah, Dr. Wan Norailiana Wan Ab Rahman, Dr. Fadzidah Mohd Idris, Dr. Idza Riati Ibrahim, Dr. Muhammad Syazwan Mustaffa, Dr. Alex See, Mr. Muhammad Misbah Muhamad Zulkimi, Mr. Ikhwan and Mr. Che Sulaiman Ahmad, who helped me by creating a stimulating and exciting working atmosphere, by sharing their views and advice and by organising and participating in all the events. There were many fun times, sometimes needed to take my mind off the research or get perspective on things. I will always remember and cherish those times.

I take this opportunity to sincerely acknowledge Ministry of Higher Education Malaysia for providing financial assistance through myBrain15 scholarship which supported me to pursue my research conveniently.

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

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

UPM	Universiti Putra Malaysia
$SrTiO_3$, ST	Strontium titanate
$CaCu_3Ti_4O_{12}$,CCTO	Calcium Copper Titanate
ε''	Dielectric constant
Tan δ	Loss Tangent
Hz	Hertz
BPR	Ball to powder weight ratio
CCTO-ST	Strontium Titanate-doped Calcium Copper Titanate
vol.	Volume
wt.	Weight
Z	Impedance
M	Electric Modulus
Y	Admittance
PVA	Polivinyl Alcohol
E_a	Activation Energy
Ω	Ohm
DC	Direct current
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
FESEM	Field Emission Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
ρ	Density
ρ_{xrd}	X-ray density
P_{exp}	Experimental density

CHAPTER 1

INTRODUCTION

1.1 Background of the study

On 7 March 2014, marketsandmarkets.com published a report titled "Dielectric Material Market by Technology (OLED, LED, TFT-LCD, LED-LCD, Plasma, LCOS, DLP), Application (Conventional, 3D, Transparent, Flexible), Material (Metal Oxide, a-Silicon, LTPS, PET, PEN, Photonic Crystals) & by Geography - Global Forecast to 2013 - 2020". Analysis of the report shows that the total dielectric materials market is projected to reach market revenue worth $50.63 billion by 2020 (marketsandmarkets.com, 2014). According to this analysis, it can be concluded that the role of dielectric display materials in display panels has evolved so as to meet the changing requirements of the new and more advanced chip designs and packaging technologies. Dielectric materials are an integral part of the display panels that define the nature and the role of the displays. A lot of research directed at improving materials properties was done over the years. The progress in this field is very rapid.

Owing to the need of modern electronic industry, the synthesis methods are used to control the morphology and grain size of material. Among these methods, mechanical alloying (MA) is one of the methods that are often used to synthesize materials and can effectively control the morphology and grain size of products (Suryanarayana & Froes, 1992) MA is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill (Suryanarayana, 2001). It is also an economical process with important technical advantages. The usefulness of this method was well documented in literature and excellent reviews and monographs are available dealing with the different aspects. It is well established that the properties and behaviour of every material is dependent on its microstructure, and that microstructure can be controlled by the way in which the material is made and processed. Properties of dielectric materials are affected by their microstructures, especially grain size, porosity and density, which in turn, are strongly influenced by sintering temperature. With increasing sintering temperature, grain size and porosity will exhibit different development trends, which strongly influence their dielectric properties. Thus, it is important to correlate the microstructure and dielectric properties of materials relating them from nanometre grain-size microstructure until they have evolved to their final forms at their last evolution stage.

1.2 Dielectric Materials

Dielectric materials play a key role in our global society with a wide range of applications, from terrestrial and satellite communication including software, radio, GPS, and DBS TV to environmental monitoring via satellite. The last decade witnessed a well-paced transformation in the display technology market and is expected to grow further. Products such as smartphones, laptops, tablets, and TVs are garnering a very high demand from the consumers' perspective; this demand directly impacts the ever-increasing demand for the materials associated with these products.

A material is classified as "dielectric" if it has the ability to store energy when an external electric field is applied. There were no studies about the properties of insulating materials until 1837. Throughout most of the 19th century, scientists searching for insulating materials for specific applications have become increasingly concerned with the detailed physical mechanism governing the behavior of these materials. After more than eighty years of development, the theory of dielectrics is still an active area for research. Understanding the behaviour of dielectric materials with the variations of field, temperature and frequency is of particular importance for present day electronics.

In recent years, a lot of researches and attempts were conducted to find ingenious and readily available dielectric materials that could yield predictable and controllable permittivity with very low dielectric loss factor has always proved to be positive and successful. As for that, much attention was paid to $CaCu_3Ti_4O_{12}$ (CCTO) (Homes et al., 2001; Subramanian et al., 2000; Ramirez et al., 2000), which exhibits a high dielectric constant with good temperature stability. The dielectric properties of CCTO were first reported by Subramanian et al. in 2000. They first reported that large dielectric constants were found in $ACu_3Ti_4O_{12}$ (A= trivalent rare earth or Bi) type material. CCTO, displaying the most special behavior, shows a dielectric constant of about 12,000 at 1 kHz, remaining steady in a large temperature range, from 100 K to 400 K . As we know, some materials with dielectric constants higher than 1,000 are associated with ferroelectric properties and the dielectric constant changes greatly during the ferroelectric phase transition. This property limits their applications in industry because, often it is required that the dielectric constant of the material is fairly independent of temperature. Therefore, CCTO with its low dependence on temperature is of great interest to us.

Even though CCTO has a large permittivity, its relatively high dielectric loss is one of the main problems regarding the use of CCTO in practical applications. In particular, an enhancement of ε is usually accompanied by an increase in dielectric loss. It is essential to decrease the dielectric loss if CCTO ceramics are to be introduced into commercial applications. Some research results showed that the dielectric loss in CCTO ceramics mainly originates from semiconducting grains and insulating grain boundaries. Numerous attempts were made to reduce the current leakage by modifying the semiconducting properties and interfacial structure of CCTO ceramics. One effective approach is to combine the high-dielectric constant materials with another insulating oxide with low tangent loss to improve the final materials characteristics.

Perovskite-type oxides are some of the materials with high dielectric constant. The ability of the simple perovskite structure (ABO_3) to give rise to intergrowth structures, oxygen deficient structures and ordered perovskite structures are well known (Rao and Thomas, 1985; Anderson and Poeppelmeier, 1991; Anderson et al., 1993). Among the wider family of perovskite-type oxides, $SrTiO_3$ (ST) is a representative member of this family; it displays a cubic structure. ST is a ceramic material with high dielectric constant (ε_r'), low dielectric loss (ε_r"), large polarization and good insulating properties is a potential candidate in the electronic industry. ST has a low dielectric loss as an incipient ferroelectric, though it does not possess attractive properties in pure form. Therefore, it would be interesting to add a small amount of ST to CCTO and investigate the dielectric and electrical properties of such composite materials. Thus, it is important to correlate the microstructure and dielectric properties of CCTO, ST and CCTO-ST relating them from nanometre grain-size microstructure until they have evolved to their final forms at their last evolution stage.

1.3 Problem Statement

Most of the works carried out on CCTO-ST system basically cover the composition of CCTO-ST towards their electrical properties, effect of doping and their dielectric and microstructure relationship at higher sintering temperatures. To the best of our knowledge, reports on microstructure-property evolution study of CCTO-ST which endeavour to correlate the evolving microstructure with the dielectric properties have not been given in details. In order to obtain greater clarification on this aspect; an attempt is made in this work to synthesize CCTO-ST powders by mechanical alloying method which is followed by compacted-sample sintering in a series of ascending temperatures. Thus this research embarks on the following questions:

- What would be the dielectric-microstructure relationships at various intermediate sintering conditions during the parallel evolutions of the morphology and dielectric properties?
- Do the changes of microstructure affect the dielectric properties of the materials?
- How do dielectric properties evolve with the microstructure changes?

1.4 Objectives

1.4.1 Main Research-Project Objective

The main goal of this research is to critically track the evolution of the dielectric properties parallel to the microstructural changes starting from unusually low sintering temperature up to its final form. Previous literature has shown little evidence of synthesis work via high energy ball milling to reach nanometer grain-size region and critically track the microstructural grain growth to micron size. Thus, due to the significant amount of materials required, mechanical alloying seems to be the only practical technique in studies involving the evolution of the microstructure of the material.

1.4.2 Work-step Objectives

The work steps of the project are to ensure the successful attainment of the project objective. These are:

i) To synthesize CCTO, ST and ST doped CCTO via mechanical alloying
ii) To study the effect of sintering temperature on the evolving microstructural changes.
iii) To study the dielectric behaviour of the samples
iv) To study the dopant effect on microstructure-dielectric properties

1.5 Limitations of the study

Although the objectives and scopes in this thesis had been thoroughly investigated and studied, there are few limitations regarding to the research:

i. The Dielectric measurement was carried out in the 40 Hz - 1MHz due to the limitation in experimental equipment constrained.

1.6 Thesis Outline

This thesis comprises of 6 chapters. In the first chapter, general introduction of evolution and materials study, microstructural-dielectric properties and some research questions are discussed. The second chapter deals with literatures of the synthesis methods, mechanical alloying and important materials properties, dielectric theory and materials properties, some microstructural consideration on dielectric properties and some overview about materials evolution studies. The third chapter presents the basic theories on titanates and sintered materials. In some aspects of the theory, the chapter describes the basic crystal structure that controls the behavior of the dielectric materials. Experimental and measurement techniques which include sample preparation and the apparatus used for both microstructural-dielectric analyses were discussed in the fourth chapter. The fifth chapter presents the results of microstructural-dielectric analysis. The ceramics were analysed using XRD, SEM, EDX, and TEM, leading to the understanding of the microstructure evolution observed. Data obtained from dielectric measurements were also discussed. The sixth or final chapter summarizes and concludes the research findings and comments on the system in relation to microstructural-dielectric properties. Recommendations for further work are also given. The author's biography, appendices and references/bibliographies are in the last part of the thesis.

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