

STRUCTURE CHARACTERIZATION AND SURFACE MORPHOLOGY OF  
LOW SINTERING TEMPERATURE SYNTHESIZED CALCIUM TITANATE  
CERAMICS

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*To my beloved parents, Mr. Jailani Dimin and Mdm. Esah Salleh, siblings, friends  
and my dedicated supervisor, Dr. Wan Nurulhuda Wan Shamsuri*

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## ABSTRACT

The purpose of this study is to investigate the effects of calcination temperature on the structure and surface morphology of calcium titanate ( $\text{CaTiO}_3$ ) ceramics. The structure and composition of pre-sintered  $\text{CaTiO}_3$  powder and sintered  $\text{CaTiO}_3$  ceramic samples were analyzed by x-ray diffraction (XRD). The crystallite size of the samples was also analyzed by XRD. Scanning electron microscope (SEM) was used to analyze the surface morphology of the samples. The chemical compositions were determined by energy dispersive x-ray spectroscopy (EDX). The density of ceramic samples was measured by Archimedes' method. XRD analysis shows that calcium carbonate ( $\text{CaCO}_3$ ) starts to react with titanium dioxide ( $\text{TiO}_2$ ) at temperature of  $600^\circ\text{C}$  and the size of  $\text{CaTiO}_3$  crystallite increases with the increase of calcination temperature. The micrograph images from SEM show that elongated particles are present in the pre-sintered powder samples. They are identified by EDX as  $\text{CaCO}_3$  particles, which shrunk in size as the calcination temperature increases. Besides, pores that contribute to the reduction in density are also observed in the micrograph images of sintered ceramic samples from SEM. The percentage density of sintered ceramic samples increases from 83.6% to 85.0% with the increasing of the pre-sintering temperature.

## ABSTRAK

Tujuan kajian ini adalah untuk mengkaji kesan suhu pengkalsinan terhadap struktur dan morfologi permukaan seramik kalsium titanat ( $\text{CaTiO}_3$ ). Struktur dan komposisi sampel serbuk  $\text{CaTiO}_3$  pra-tersinter dan seramik  $\text{CaTiO}_3$  tersinter dianalisis menggunakan belauan sinar-x (XRD). Saiz hablur sampel juga dianalisis menggunakan XRD. Mikroskop elektron pengimbas (SEM) digunakan untuk menganalisis morfologi permukaan sampel. Komposisi kimia ditentukan oleh spektroskopi serakan tenaga sinar-x (EDX). Ketumpatan sampel seramik diukur menggunakan kaedah Archimedes. Analisis XRD menunjukkan kalsium karbonat ( $\text{CaCO}_3$ ) mula bertindak balas dengan titanium dioksida ( $\text{TiO}_2$ ) pada suhu  $600^\circ\text{C}$  dan saiz hablur  $\text{CaTiO}_3$  meningkat dengan peningkatan suhu pengkalsinan. Imej mikrograf SEM menunjukkan bahawa terdapat zarah memanjang dalam sampel serbuk pra-tersinter. Zarah berkenaan telah dikenal pasti dengan EDX sebagai  $\text{CaCO}_3$ , yang mengecut apabila suhu pengkalsinan meningkat. Selain itu, liang yang menyumbang kepada pengurangan ketumpatan seramik juga diperhatikan dalam imej mikrograf SEM bagi sampel seramik tersinter. Peratusan ketumpatan bagi sampel seramik tersinter meningkat daripada 83.6% kepada 85.0% dengan peningkatan suhu pra-tersinter.

**TABLE OF CONTENTS**

<b>CHAPTER</b>	<b>TITLE</b>	<b>PAGE</b>
	<b>DECLARATION</b>	i
	<b>DEDICATION</b>	ii
	<b>ACKNOWLEDGEMENT</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	x
	<b>LIST OF FIGURES</b>	xi
	<b>LIST OF SYMBOLS</b>	xv
<b>1</b>	<b>INTRODUCTION</b>	
	1.1 Background of Study	1
	1.2 Problem Statement	2
	1.3 Objectives of Study	3
	1.4 Scope of Study	4
	1.5 Significance of Study	5
<b>2</b>	<b>LITERATURE REVIEW</b>	
	2.1 Introduction	6
	2.2 Calcium Titanate	6
	2.3 Synthesis of Calcium Titanate	9
	2.3.1 Calcinations	9
	2.3.2 Sintering Process	13

2.4	The Structure Characterization of CaTiO <sub>3</sub>	15
2.4.1	Crystallite Size	23
2.4.2	Lattice Strain	26
2.5	The Density of CaTiO <sub>3</sub> Ceramics	27
2.6	Analyses Instruments	29
2.6.1	X-ray Diffraction	30
2.6.2	Scanning Electron Microscope	31
2.6.3	Energy-Dispersive X-ray Spectroscopy	33
2.6.4	Archimedes' Principle	36
<b>3</b>	<b>METHODOLOGY</b>	
3.1	Introduction	38
3.2	Research Instruments	38
3.3	Preparation of Samples	41
3.4	Characterization of Samples	45
3.4.1	X-ray Diffraction Measurement	45
3.4.2	Scanning Electron Microscopy Imaging	46
3.4.3	EDX Spectrum Measurement	48
3.4.4	Archimedes' Principle	48
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	
4.1	Introduction	50
4.2	Appearance of CaTiO <sub>3</sub>	50
4.3	X-Ray Diffraction Analyses	52
4.3.1	Structure and Composition	53
4.3.2	Crystallite Size	60
4.3.3	Lattice Strain	61
4.4	Surface Morphology Analyses	65
4.5	Elemental Analyses	70
4.6	Ceramics Density Measurement	72



<b>5</b>	<b>CONCLUSIONS AND SUGGESTIONS</b>	
5.1	Conclusions	74
5.2	Suggestions	76
	<b>REFERENCES</b>	77

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Data obtained by XRD analyses of CaTiO <sub>3</sub> powders (Cavalcante <i>et al.</i> , 2008)	25
3.1	Calcining temperature, heating rate and dwell time for each pre-sintered sample	43
3.2	Sintering temperature, heating rate and dwell time for sintered samples	44
4.1	Entry numbers and estimated quantity (wt. %) of pre-sintered powder samples measured by Match! software	55
4.2	Information of plane and angle of CaCO <sub>3</sub> (calcite), TiO <sub>2</sub> (anatase) and CaTiO <sub>3</sub> (perovskite) for pre-sintered powder samples	56
4.3	Entry numbers and estimated quantity (wt. %) of sintered ceramics samples measured by Match! software	58
4.4	Information of plane and angle of CaCO <sub>3</sub> (calcite), TiO <sub>2</sub> (anatase) and CaTiO <sub>3</sub> (perovskite) for sintered ceramics samples	58
4.5	Crystal system and lattice parameters of sintered CaTiO <sub>3</sub> ceramics	60
4.6	EDX results of pre-sintered CaTiO <sub>3</sub> powder samples	71
4.7	Density and relative density of sintered CaTiO <sub>3</sub> ceramics samples with their calcinations temperature	72

## LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Part of periodic table which shows position of Ca, Ti, and O	7
2.2	Schematic illustration of the perovskite-type crystal structure of $ABO_3$ (Kamiya <i>et al.</i> , 2006)	8
2.3	Decomposition curve of nano $CaCO_3$ (Zhu <i>et al.</i> , 2011)	10
2.4	TG/DTA of the powder mixtures of $CaCO_3$ and $TiO_2$ (Branković <i>et al.</i> , 2007)	11
2.5	Solid-state reaction between $CaCO_3$ and $TiO_2$ where (a) is the original interface of $CaCO_3$ - $TiO_2$ , (b) the nucleation at the interface and (c) diffusion path of $CaCO_3$ and $TiO_2$ at product layer	12
2.6	Illustration of pore-drag grain growth (Sakuma, 1996)	13
2.7	Particles rearrangement and growth during sintering process (Lame <i>et al.</i> , 2003)	14
2.8	The (a) initial, (b) intermediate and (c) final stages of sintering (Ring, 1996)	15
2.9	Slightly-distorted perovskite experimental room-temperature structure of $CaTiO_3$ (Cockayne and Burton, 2000)	16
2.10	XRD patterns for $TiO_2$ - $CaCO_3$ mixture samples before and after thermal treatment at $1100^\circ C$ . Major peaks are noted for anatase (A), rutile (B), calcite (C), lime (D) and perovskite (E) (Mergos <i>et al.</i> , 2006)	17

2.11	A selected part of neutron diffraction patterns of $\text{CaTiO}_3$ measured at different temperatures from 296 K to 1720 K on heating, showing the orthorhombic plane of (0 2 0), (1 1 2), (2 0 0), (1 2 0), (2 1 0), (1 2 1), (1 0 3), and (2 1 1) reflections between 296 K and 1473 K; the tetragonal plane of (1 1 2), (2 0 0), and (2 1 1) reflections between 1523 K and 1622 K; and the cubic plane of (1 1 0) reflection between 1647 K and 1720 K (Yashima and Ali, 2009)	18
2.12	XRD patterns of (a) the $\text{CaTiO}_3$ ceramic and (b) the JCPDS data 42-0423 for orthorhombic $\text{CaTiO}_3$ (Hu <i>et al.</i> , 2011)	19
2.13	XRD patterns of $\text{CaTiO}_3$ powders heat treated at different temperatures for 120 min in conventional furnace under air atmosphere (Cavalcante <i>et al.</i> , 2008)	20
2.14	XRD pattern of the as-synthesized product with all its diffraction peaks can be readily indexed to orthorhombic structure $\text{CaTiO}_3$ (JCPDS card no. 82-0229) (Li <i>et al.</i> , 2011)	21
2.15	XRD patterns of a CaO-anatase $\text{TiO}_2$ mixture created by using a planetary ball mill (Park and Kim, 2010)	22
2.16	X-ray powder diffraction patterns showing the transformation of a mixture of CaO and the anatase modification of $\text{TiO}_2$ to $\text{CaTiO}_3$ as a function of time (Berry <i>et al.</i> , 2001)	23
2.17	An example of $\text{CaTiO}_3$ peak from sample C7 that was corrected using ‘Gaussian Fit’	24
2.18	Average crystallite sizes as a function of heat treatment of $\text{CaTiO}_3$ powders for 120 min in conventional furnace. The vertical bars show the standard mean error (Cavalcante <i>et al.</i> , 2008)	25
2.19	Plot of $\beta_r \cos \theta$ versus $\sin \theta$ graph	27
2.20	Density as a function of sintering temperature (Pickup, 1992)	28

2.21	Density of CaTiO <sub>3</sub> ceramics after 6 hours sintering (Liou <i>et al.</i> , 2009)	29
2.22	Schematic diagrams for measurement of $\theta$ from $2\theta$	30
2.23	Schematic diagram of SEM	31
2.24	Illustration of several signals generated by the electron beam-specimen interaction (Zhou and Wang, 2007, pp. 3)	32
2.25	(a) Optical photograph of facet lens on the compound eye of butterfly <i>Euploea mulciber</i> . (b) SEM image of the facet lens on the compound eye (Lou <i>et al.</i> , 2012)	33
2.26	EDX spectrum of CaTiO <sub>3</sub> : Pr <sup>3+</sup> (Peng <i>et al.</i> , 2010)	34
2.27	Principal quantum number (n) order of the inner structure of atom	35
2.28	Electron from higher-energy shell drops to lower energy shell	36
3.1	The research flow of this study	40
3.2	Starting CaCO <sub>3</sub> -TiO <sub>2</sub> powder mixtures in ethanol	41
3.3	Starting CaCO <sub>3</sub> -TiO <sub>2</sub> mixtures after dried overnight	42
3.4	Flow diagram of CaTiO <sub>3</sub> ceramic synthesis method	44
3.5	High Resolution Diffractometer Bruker D8 Advance for XRD measurements	46
3.6	Hitachi TM3000 TableTop scanning electron microscope for surface morphology	47
3.7	JOEL JSM-6390LV scanning electron microscope for surface morphology	47
3.8	Analytical balance with specific density apparatus	49
4.1	Ceramic sample (a) before and (b) after sintering process	51
4.2	Cross-section of a ceramic sample	52
4.3	XRD patterns of pre-sintered powders of untreated (C1), 400°C (C2), 500°C (C3), 600°C (C4), 700°C (C5), 800°C (C6) and 900°C (C7) calcined samples ( $\Delta$ = anatase (TiO <sub>2</sub> ), $\diamond$ = aragonite (CaCO <sub>3</sub> ), $\blacklozenge$ = calcite (CaCO <sub>3</sub> ), and $\bullet$ = perovskite (CaTiO <sub>3</sub> ))	53

4.4	XRD patterns of compacted $\text{CaTiO}_3$ after sintering at 900°C where S1 is previously untreated, S6 and S7 were previously treated at calcinations temperature of 800°C and 900°C respectively ( $\Delta$ = anatase ( $\text{TiO}_2$ ), $\nabla$ = rutile ( $\text{TiO}_2$ ), and $\bullet$ = perovskite ( $\text{CaTiO}_3$ ))	57
4.5	Peak shifts to lower angle	59
4.6	Graph of crystallite size of $\text{CaTiO}_3$ versus calcination temperature	61
4.7	Plots of $\beta_r \cos \theta$ versus $\sin \theta$ for pre-sintered powder samples which were calcined at temperature of (a) 700°C, (b) 800°C and (c) 900°C	62
4.8	Lattice strain of pre-sintered $\text{CaTiO}_3$ powder samples in a function of calcinations temperatures	63
4.9	Plots of $\beta_r \cos \theta$ versus $\sin \theta$ for sintered $\text{CaTiO}_3$ ceramics samples where (a) S1, (b) S6 and (c) S7	64
4.10	Lattice strain of sintered $\text{CaTiO}_3$ ceramics samples in a function of pre-sintering temperatures	65
4.11	SEM images of agglomerate of pre-sintered powder samples which were calcined at (a) 800°C and (b) 900°C	66
4.12	SEM images of pre-sintered $\text{CaTiO}_3$ powder samples which were calcined at a) 400°C, b) 500°C, c) 600°C, d) 700°C, e) 800°C, and f) 900°C	67
4.13	Schematic diagram of the $\text{CaCO}_3$ shrinkage	68
4.14	SEM images of sintered $\text{CaTiO}_3$ ceramics samples which previously (a) untreated, (b) calcined at 800°C and (c) calcined at 900°C	69
4.15	EDX spectrum of pre-sintered $\text{CaTiO}_3$ powder samples which were calcine at (a) 400°C, (b) 500°C, (c) 600°C, (d) 700°C, (e) 800°C and (f) 900°C	70
4.16	Graph of relative density of sintered $\text{CaTiO}_3$ ceramics samples for sintering temperature of 900°C	73

## LIST OF SYMBOLS

$ABX_3$	-	General formula of perovskite unit cell
BET	-	Brunauer-Emmett-Teller
$B$	-	peak width
$^{\circ}C$	-	degree celcius
$D$	-	average crystallite size
$d_{hkl}$	-	interplanar spacing
EDX	-	energy-dispersive X-ray spectroscopy
F	-	force
h	-	hour
K	-	Kelvin
$K$	-	shape factor of the average crystallite size (expected shape factor is 0.9)
Mw	-	molecular weight
n	-	principal quantum number
$n$	-	order of reflection
$\eta$	-	strain
$\sigma$	-	standard deviation
P	-	pressure
$\rho$	-	density
SEM	-	scanning electron microscope
$\theta$	-	diffraction angle
$\theta_i$	-	incident beam angle
$\theta_r$	-	scattered beam angle
$\lambda$	-	X-ray wavelength
wt%	-	weight percent

WD	-	working distance
XRD	-	X-ray diffraction
z	-	atomic number



## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

Since the discovery of a perovskite material by Gustav Rose in the Ural Mountains of Russia in 1839, this material has made its own way in various fields of research and application. Perovskite oxide materials are excellently exhibiting interesting physical properties including dielectric, ferroelectric and luminescence (Lemanov *et al.*, 1999; Grinberg *et al.*, 2013; Park *et al.*, 2014). The different in their physical properties are related to phase transitions, which in turn are sensitive to variables such as grain size, purity, chemical composition, number of surface and bulk defects, and sintering conditions. For example, X-ray diffraction data of a study conducted by Grinberg *et al.* (2013) shows a gradual transition from the orthorhombic ferroelectric potassium niobate (KNO) structure to a cubic structure as the chemical composition was changed.

The unique properties of perovskite materials have attract the attention of researchers to manipulate their structure and composition so that these materials can be served as ceramics, electronics, catalysts or even superconductor (Patterson, 2012;

Zhu *et al.*, 2014; Rubel *et al.*, 2014). Most of the useful ferroelectric and piezoelectric materials in industrial use are derived from the perovskite structure.

All this time, many synthesis methods have been explored as encouraged by the great demand of industrial applications. Various methods have been proposed and developed for preparation of perovskite powder such as solid-state reaction, wet-chemical, sol-gel, mechanical and chemical methods amongst others. Chemical methods is seems to be the best synthesis method compared to other methods as it has advantages such as high-purity, homogeneity and precise composition. Nevertheless, most of these chemical methods have complicated procedures involved and not cost-effective due to the requirement of high-purity precursor compounds that are sometimes more expensive than the widely available oxides and carbonates.

In this study, experiments on widely used methods such as solid-state reaction involving synthesizing at various calcinations temperature to produce the perovskite powders were conducted and analyzed to determine if the processes can possibly resulted in the production of perovskite powder suitable for perovskite ceramics fabrication.

## 1.2 Problem Statement

At this moment in microelectronic industry, advanced ceramics became the key of success for the development of integrated circuits. In the future, calcium titanate ( $\text{CaTiO}_3$ ) could be of major use in this field of applications. In spite of that, pure  $\text{CaTiO}_3$  ceramics are difficult to densify and too fragile for many practical applications. Therefore, research on preparation of  $\text{CaTiO}_3$  ceramics starting from the synthesis of  $\text{CaTiO}_3$  powders is interesting to study. Synthesis method of  $\text{CaTiO}_3$  powders has played a significant role in determining the properties of  $\text{CaTiO}_3$

ceramics. Mixing two or more materials powder followed by heat treatment processes may change the properties of the mixed powder. It is known that heat treatment capable of changing structural properties of materials. Normally,  $\text{CaTiO}_3$  ceramics are produced via solid-state reaction by sintering starting  $\text{CaCO}_3$  and  $\text{TiO}_2$  powders mixture at high sintering temperature. However, the high temperature causes inhomogeneity and contamination by impurity in final products (Evans *et al.*, 2003). On the other side, calcinations process have been used as pre-sintering process in solid-state reaction to reduce the sintering temperature, however, the effects of calcining the starting mixed  $\text{CaCO}_3$ - $\text{TiO}_2$  powders prior to sintering process have received less attention. According to Mousavi (2014), “the more important processes that influences the product characteristics and properties are powder preparation, powder calcining and sintering”.

It remains a great challenge to obtain pure  $\text{CaTiO}_3$  phase with simple process, low cost and high sinterability. Optimizing the powder preparation process is necessary to obtain pure  $\text{CaTiO}_3$  ceramics. Heat treatment is one of the factors that can affect the micro-structure of  $\text{CaTiO}_3$  powders, which in turn affect the micro-structure and sinterability of  $\text{CaTiO}_3$  ceramics. Sinterability is “a property of the material to densify during heating” (Shoulders, 2009). This study is conducted to explore the potency of preparing pure  $\text{CaTiO}_3$  ceramics using sintering temperature of  $900^\circ\text{C}$  with simple powder preparation, which prior calcinations was used as pre-sintering process. Structural, morphological, elemental composition and sinterability properties of  $\text{CaTiO}_3$  in form of powders and ceramics will be studied.

### 1.3 Objectives of Study

The objectives of this study are:

- i) To determine the structure characterization, elemental composition and surface morphology of  $\text{CaTiO}_3$  powders prepared by solid-state reaction,

- ii) To determine the effects of pre-sintering process on structural, surface morphology and density of sintered  $\text{CaTiO}_3$  ceramics,
- iii) To investigate the potency of calcinations as pre-sintering process in increasing the density of sintered  $\text{CaTiO}_3$  ceramics.

#### 1.4 Scope of Study

Sintered  $\text{CaTiO}_3$  ceramic are fabricated using solid-state reaction. Seven samples of pre-sintered  $\text{CaTiO}_3$  powder are prepared first by mixing  $\text{CaCO}_3$  and  $\text{TiO}_2$  powders before fabricated into ceramic. Six of the pre-sintered  $\text{CaTiO}_3$  powder samples are calcined at different calcinations temperature between  $400^\circ\text{C}$  and  $900^\circ\text{C}$  at  $100^\circ\text{C}$  interval. The other one powder sample is remained untreated. Calcination is applied to decomposing  $\text{CaCO}_3$ , so the samples with no or very small amount of  $\text{CaCO}_3$  trace are chosen to fabricate the ceramics. A ceramic that is fabricated from sintering the untreated powder sample is used to compare its results with the sintered ceramic samples with prior calcinations process. Therefore, the effect of calcinations as pre-sintering process on the sintered  $\text{CaTiO}_3$  ceramic samples could be determined. Structural characterization, especially materials composition, phase change, and crystallite size, are examined using XRD. Surface morphologies of pre-sintered  $\text{CaTiO}_3$  powder and sintered  $\text{CaTiO}_3$  ceramic samples are observed by SEM. Lastly, Archimedes' method is used to measure the density of sintered  $\text{CaTiO}_3$  ceramics. Most of the preparation and characterization of samples are performed in laboratories in Universiti Teknologi Malaysia.

## **1.5 Significance of Study**

This study is important for other researchers who are interested in perovskites and ceramics materials. This study implemented a synthesis process approach to obtain a pure and high-density ceramics using solid-state reaction at low sintering temperature. Fabrication of  $\text{CaTiO}_3$  ceramics with the aid of prior calcinations as pre-sintering process gives them another alternative to produce  $\text{CaTiO}_3$  ceramics at sintering temperature lower than  $1000^\circ\text{C}$ .

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