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 ($CaTiO_3$) ceramics. The structure and composition of pre-sintered $CaTiO_3$ powder and sintered $CaTiO_3$ 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 ($CaCO_3$) starts to react with titanium dioxide (TiO_2) at temperature of 600°C and the size of $CaTiO_3$ 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 $CaCO_3$ 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 ($CaTiO_3$). Struktur dan komposisi sampel serbuk $CaTiO_3$ pra-tersinter dan seramik $CaTiO_3$ 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 ($CaCO_3$) mula bertindak balas dengan titanium dioksida (TiO_2) pada suhu 600°C dan saiz hablur $CaTiO_3$ 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 $CaCO_3$, 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.

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LIST OF SYMBOLS

ABX_3	-	General formula of perovskite unit cell
BET	-	Brunauer-Emmett-Teller
B	-	peak width
°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
η	-	strain
σ	-	standard deviation
P	-	pressure
ρ	-	density
SEM	-	scanning electron microscope
θ	-	diffraction angle
θ_i	-	incident beam angle
θ_r	-	scattered beam angle
λ	-	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 ($CaTiO_3$) could be of major use in this field of applications. In spite of that, pure $CaTiO_3$ ceramics are difficult to densify and too fragile for many practical applications. Therefore, research on preparation of $CaTiO_3$ ceramics starting from the synthesis of $CaTiO_3$ powders is interesting to study. Synthesis method of $CaTiO_3$ powders has played a significant role in determining the properties of $CaTiO_3$

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, $CaTiO_3$ ceramics are produced via solid-sate reaction by sintering starting $CaCO_3$ and 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 $CaCO_3$-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 $CaTiO_3$ phase with simple process, low cost and high sinterability. Optimizing the powder preparation process is necessary to obtain pure $CaTiO_3$ ceramics. Heat treatment is one of the factors that can affect the micro-structure of $CaTiO_3$ powders, which in turn affect the micro-structure and sinterability of $CaTiO_3$ 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 $CaTiO_3$ ceramics using sintering temperature of 900°C with simple powder preparation, which prior calcinations was used as pre-sintering process. Structural, morphological, elemental composition and sinterability properties of $CaTiO_3$ 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 $CaTiO_3$ powders prepared by solid-state reaction,

ii) To determine the effects of pre-sintering process on structural, surface morphology and density of sintered $CaTiO_3$ ceramics,

iii) To investigate the potency of calcinations as pre-sintering process in increasing the density of sintered $CaTiO_3$ ceramics.

1.4 Scope of Study

Sintered $CaTiO_3$ ceramic are fabricated using solid-state reaction. Seven samples of pre-sintered $CaTiO_3$ powder are prepared first by mixing $CaCO_3$ and TiO_2 powders before fabricated into ceramic. Six of the pre-sintered $CaTiO_3$ powder samples are calcined at different calcinations temperature between 400°C and 900°C at 100°C interval. The other one powder sample is remained untreated. Calcination is applied to decomposing $CaCO_3$, so the samples with no or very small amount of $CaCO_3$ 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 $CaTiO_3$ ceramic samples could be determined. Structural characterization, especially materials composition, phase change, and crystallite size, are examined using XRD. Surface morphologies of pre-sintered $CaTiO_3$ powder and sintered $CaTiO_3$ ceramic samples are observed by SEM. Lastly, Archimedes' method is used to measure the density of sintered $CaTiO_3$ 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 $CaTiO_3$ ceramics with the aid of prior calcinations as pre-sintering process gives them another alternative to produce $CaTiO_3$ ceramics at sintering temperature lower than 1000°C.

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