THE STUDY OF MAGNESIUM-DOPED CALCIUM COPPER TITANATE ($CaCu_3Ti_4O_{12}$) EFFECT TO THE MICROSTRUCTURAL AND ELECTRICAL PROPERTIES OF $Ca(Cu_{3-x}Mg_x)Ti_4O_{12}$

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
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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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Date	:

STUDENT'S DECLARATION

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.

Signature :

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LIST OF SYMBOLS

Å	Angstrom (10^{-10})
ω	Angular frequency
~	Approximately
^{o}C	Degree celcius
ε’	Dielectric permittivity
ε”	Dielectric loss
F	Farad
g	Grams
Hz	Hertz
h	Hour
µ	Micron (10^{-6})
ml	Milliliter

LIST OF ABBREVIATIONS

CCTO	-	Calcium copper titanate
FESEM	-	Field emission scanning microscopy
PVA	-	Polyvinyl alcohol
XRD	-	X-ray diffraction

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ABSTRACT

In this work, calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) with magnesium oxide, MgO composition of x = 0, 0.05 and 0.3 were prepared using the solid-state reaction method. Substitution of magnesium, Mg was seen to give slight changes to microstructure of CCTO ceramics, doping with small amount of Mg (x = 0.05) results in smaller grain size of ~2.54 μm, while doping with large amount of Mg (x = 0.3) promotes grain growth ~30 μm. The doping effect of Mg to CCTO was seen to be able to increase the dielectric permittivity with maximum dielectric permittivity shown by x = 0.05, ~ 4.53×10^6 at 1 kHz. However, the doping effect of Mg was not able to reduce the dielectric loss. The lowest dielectric loss at frequency 1 kHz obtained was shown by pure CCTO with a value of 0.014. Even though Mg-doped CCTO ceramics shows larger dielectric loss than pure CCTO, the amount obtained was lower compared to other research that uses MgO as dopant.

ABSTRAK

Dalam karya ini, kalsium kuprum titanate, $CaCu_3Ti_4O_{12}$ (CCTO) dengan komposisi magnesium oksida, MgO x = 0, 0.05 dan 0.3 telah dihasilkan dengan menggunakan kaedah tindak balas keadaan pepejal. Penggantian magnesium, Mg ke dalam kuprum, Cu telah menyebabkan sedikit perubahan kepada struktur mikro seramik CCTO, apabila jumlah komposisi MgO kecil (x = 0.05), saiz struktur mikro seramik mengecil sehingga ~2.54 μm, tetapi apabila komposisi MgO ditambah kepada x = 0.3, saiz struktur mikro seramik meningkat kepada ~30 μm. Penambahan MgO kepada CCTO seramik juga dilihat mampu meningkatkan ketelusan dielektrik dengan komposisi x = 0.05, ketelusan dielektrik yang dihasilkan adalah setinggi ~ 4.53×10^6 pada frekuensi 1 kHz. Walaubagaimanapun, penambahan MgO kepada CCTO seramik tidak berjaya untuk mengurangkan kehilangan dielektrik. Kehilangan dielektrik paling rendah didapati pada CCTO seramik dengan komposisi x = 0, iaitu 0.014 pada frekuensi 1 kHz. Walaupun CCTO yang ditambah MgO menunjukkan kehilangan dielektrik yang tinggi berbanding CCTO tulen, jumlah kehilangan dielektrik yang ditunjukkan oleh CCTO yang ditambah MgO dalam kajian ini masih rendah jika bandingkan dengan jumlah kehilangan dielektrik CCTO yang ditambah MgO oleh pengkaji lain.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF PROBLEM

Ever since the improvement of technology keeps on developing, various types of advanced ceramics have been made for different application in the industry. “Advanced ceramics” is defined as materials that have been modified in terms of its composition and internal structure in order to get the desired properties of ceramics such as superior mechanical properties, resistance to corrosion or oxidation, thermal, electrical, optical or magnetic properties to meet the demands of the industry. One of the most popular research conducted are research related to the application of advanced ceramics in electronic devices such as capacitors, insulators, substrates, integrated circuit packages, piezoelectric, magnets and superconductors (Glazer, 1972). Ceramics that are used in electronic applications are usually made from materials of oxides, nitrides, carbides and borides (Riedel and Chen, 2008).

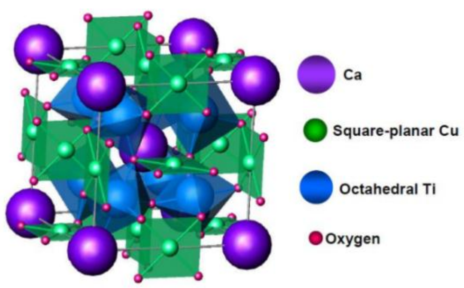

Figure 1.1 Cubic perovskite structure of CCTO

Source Schmidt and Sinclair 2013

A material that can store energy when electric field is present is called dielectric material, therefore, a material with high dielectric constant is a material with the ability of storing large amount of energy and vice versa. Calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) with body-centered cubic perovskite structure (Glazer, 1972) in Figure 1**,** is one the most popular ceramics among the researchers due to its high dielectric constant which is around 10,000 for bulk material at room temperature (Ab Rahman et al., 2014) with a good temperature stability in the range from 100 K-600 K (Subramanian et al., 2000) and almost frequency independent below 10^6 Hz (Ab Rahman et al., 2014).

These properties make CCTO a possible candidate for making microelectronic devices as it can store large amount of energy due to its large dielectric constant, ε' hence, a small size of devices for storing large amount of energy can be fabricated (Ab Rahman et al., 2014). The electrical properties of CCTO as reported by Sinclair group (cited by Sun et al., 2016) are said to be highly dependent on its internal barrier layer capacitors (ILBC) which relates to the insulating grain boundaries (GB) and semiconducting grain. From a study conducted by Pan & Bender (as cited by Yu et al., 2012), the dielectric constant of CCTO is found to be increased with the growth of grain and decrease of grain boundaries.

Even though CCTO have a very high dielectric constant, the dielectric constant, ε' also comes with a drawback of a high dielectric loss, ε'' (>0.05) (Jumpatam et al., 2014) which becomes the limiting factor for CCTO to be used for industrial application (Ab Rahman et al., 2014). Due to the high value of dielectric loss, some methods have been developed in order to overcome the problem such as, doping. Doping is a process of adding a small amount of impurities to a material with the same atomic size to improve the properties of a material (Casiday & Frey, 2016).

In this case, magnesium oxide, MgO has been chosen as the doping material due to its ability to enhance the electrical properties of CCTO by increasing the dielectric permittivity and decreasing the dielectric loss (Thongbai, Yamwong & Maensiri, 2013). In addition, the substitution of Mg^{2+} is reported to be causing the growth of grain, which leads to the increase of dielectric constant (Sun et al., 2016). The substitution of Mg^{2+} into Cu^{2+} is possible due to their close size of ionic radius as reported by Ni & Chen

(2009) and Sun et al. (2016). In this research, the effect of doping Mg^{2+} into Cu^{2+} site to the CCTO electrical and microstructural properties is observed.

1.2 PROBLEM STATEMENT

Due to its giant dielectric permittivity, much research has been made by researchers to determine the source of the giant dielectric constant and finding ways to reduce the large dielectric loss shown by CCTO. Having a large dielectric loss causes CCTO to be unsuitable for fabricating electronic devices (Xu et al., 2014) . Some of the methods used by other researchers to enhance the dielectric properties of CCTO are doping CCTO with another compound, preparing CCTO at different temperature, sintering CCTO at different conditions, and preparing CCTO with different method.

Despite the variety studies conducted, the best element to be doped in order to enhance the dielectric properties without affecting much the microstructural properties of CCTO are still an unanswered question by the researchers. In order to overcome these limitations, method of doping CCTO at the copper, Cu^{2+} site with magnesium, Mg^{2+} has been proposed due to its ability to be substituted easily to Cu^{2+} site due to the close size of atomic radius, as well as the ability to increase the dielectric constant and reduce the dielectric loss by increasing the grain size of CCTO..

1.3 OBJECTIVES OF RESEARCH

The objectives of this research are:

i) To synthesis Mg-doped CCTO using the solid-state reaction technique.
ii) To study the effect of doping Mg^{2+} in Cu^{2+} site to the growth of grains in CCTO.
iii) To increase the dielectric constant and reduce the dielectric loss of CCTO by doping Mg^{2+} in Cu^{2+} site.

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