

**DIELECTRIC PROPERTIES OF CERAMICS, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$,
SUBSTITUTED WITH Sr OR Ba**

By

FADHLINA BT CHE ROS

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of Requirement for the Degree of Master of Science**

January 2007

DEDICATION

This dedication especially goes to my husband Mohd. Fairuz SM Sharifuddin, my beloved parents Haji Che Ros and Hajjah Fatimah, my brothers, sisters and also to my friends.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Chairman: Associate Professor Wan Mohd. Daud Wan Yusoff, PhD

Faculty : Science

There has been a considerable interest in non-ferroelectric perovskite oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO). This material was discovered to possess one of the largest static dielectric constants, reaching nearly $\epsilon \sim 80,000$ for single-crystal samples at room temperature. This compound has centrosymmetric structure at room temperature with cubic space group $Im\bar{3}$. Because of such incredibly high dielectric constant, the structure, dielectric and electrical properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ substituted at Ca-site with other alkaline earth metals i.e. Ba and Sr as substitution elements were studied.

An extensive studies were carried out on the dielectric properties of the $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ and $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ where $x = 0.5, 0.52, 0.56$ and 0.6 at various temperatures. The substitutions were based on ionic radius ($r_{\text{Ca}} < r_{\text{Sr}} < r_{\text{Ba}}$) and the dielectric studies of $\text{Ca}_{1-x}\text{M}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (where $M = \text{Sr}, \text{Ba}$) have not been reported so far.

There are two categories in the experimental investigation. First, is the X-ray diffraction that is vital to provide evidence to the proposed model of dielectric behavior. Secondly, the main experiment consists of alternating current conductivity measurement where the ability to store charge (capacitance) and conductance can be investigated.

The XRD measurements reveals that the lattice parameter of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ after substitution of Sr^{2+} and Ba^{2+} changes while the pattern can be assigned to all the lines on the basis of a cubic symmetry. Single-phase for $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ was observed while for $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ it was found as multi-phase with some impurity element in the compound.

The electrical measurement was performed using High Dielectric Resolution Analyzer, measured as a function of frequency from 10^{-2} Hz to 10^6 Hz. The data collected were plotted in log-log scale of frequency against real and imaginary of permittivity and conductivity respectively. The graphs were then fitted using the universal law to obtain the properties and mechanism that took part, with parameters involved such as m , n and p . Most of the fitted graphs showed that $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ and $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ consisted of quasi-dc, dipolar mechanism, conductance G , and some R_s effect.

The substitution of Sr^{2+} and Ba^{2+} into Ca-site of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ reveals the specific behavior of this material when it is doped with a higher radius of the element. However, substitution of Sr^{2+} has apparently given the highest value of dielectric constant i.e. $\sim 2.6 \times 10^2$ when substituted by 50 mole % of Sr^{2+} at Ca-site of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**SIFAT DIELEKTRIK BAGI BAHAN PEMALAR BERASASKAN SERAMIK
CaCu₃Ti₄O₁₂ DENGAN PENGGANTIAN Sr ATAU Ba**

Oleh

FADHLINA BT CHE ROS

Januari 2007

Pengerusi: Profesor Madya Wan Mohd. Daud Wan Yusoff, PhD

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Seramik oksida bersifat bukan ferroelektrik perovskite CaCu₃Ti₄O₁₂ (CCTO) telah mendapat minat yang sewajarnya. Bahan ini didapati berjaya menghasilkan nilai pemalar dielektrik statik terbesar, menghampiri $\epsilon \sim 80,000$ untuk sampel kristal tunggal pada suhu bilik. Bahan ini mempunyai struktur simetrik pada suhu bilik dengan kumpulan kubik *Im3*. Disebabkan penghasilan sifat pemalar dielektrik tinggi yang luar biasa ini, kajian terhadap struktur dan sifat dielektrik CaCu₃Ti₄O₁₂ yang digantikan dengan kumpulan bahan alkali tanah yang lain iaitu Ba dan Sr sebagai elemen gantian pada tapak Ca.

Penyelidikan yang mendalam telah dijalankan ke atas sifat dielektrik bagi bahan Ca_{1-x}Ba_xCu₃Ti₄O₁₂ dan Ca_{1-x}Sr_xCu₃Ti₄O₁₂ dimana $x = 0.5, 0.52, 0.56$ dan 0.6 pada suhu yang berlainan. Bahan gantian adalah berasaskan jejari ion ($r_{Ca} < r_{Sr} < r_{Ba}$) dan setakat ini kajian mengenai dielektrik pada sistem Ca_{1-x}M_xCu₃Ti₄O₁₂ (M = Sr dan Ba) masih belum dilaporkan.

Terdapat dua kategori dalam kajian penyelidikan ini. Pertama, kaedah belau sinar-x yang penting untuk membuktikan struktur pada sebarang model yang dicadangkan. Kedua, kajian yang utama untuk mengukur pengaliran arus untuk mengetahui kemampuan penyimpanan cas (kapasitan) dan konduktan.

Pengukuran XRD menunjukkan bahawa parameter kekisi $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ berubah setelah diganti dengan Sr^{2+} dan Ba^{2+} sementara keputusan bentuk garisan menunjukkan bahawa ia adalah kubik simetri. Keputusan menunjukkan fasa tunggal bagi $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ dan bagi $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ adalah fasa pelbagai dan beberapa elemen tidak tulen di dalam bahan. Adalah jelas bahawa untuk mengekalkan keseragaman molekul pada tindakbalas kimia $\text{Ca}_{1-x}\text{M}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ adalah dengan mengurangkan kandungan oksigen produk.

Pengukuran sifat keelektrikan menggunakan Analisa Resolusi Dielektrik Tinggi diukur dari frekuensi 10^{-2} Hz kepada 10^6 Hz. Data yang diukur diplot pada skala log frekuensi melawan log ketelusan dan konduktiviti nyata dan khayalan. Graf-graf disuai padan menggunakan hukum universal untuk mengenal pasti sifat dan mekanisma yang terlibat, dengan parameter seperti m , n dan p . Kebanyakan graf-graf yang disuai padan menunjukkan $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ dan $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ terdiri daripada mekanisma quasi-dc, dipolar, konduktan G , dan kesan R_s .

Penggantian Sr^{2+} dan Ba^{2+} pada tapak Ca telah menunjukkan sifat tertentu bahan apabila didopkan dengan peningkatan elemen jejari ion. Bagaimanapun, penggantian Sr^{2+} telah memberikan nilai pemalar ketelapan tertinggi bagi sistem ini sehingga $\sim 2.6 \times 10^2$ apabila penggantian 50 % molekul Sr^{2+} pada tapak Ca.

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I certify that an Examination Committee met on 31st January 2007 to conduct the final examination of Fadhlina Bt. Che Ros on her Master Science thesis entitled “Dielectric Properties of High Dielectric Constant Ceramic $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Substituted With Sr, Ba” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

FADHLINA BT CHE ROS

Date: 31 MAC 2007

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