DIELECTRIC PROPERTIES OF CERAMICS, CaCu$_3$Ti$_4$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 fulfilment of the requirement for the degree of Master of Science

DIELECTRIC PROPERTIES OF CERAMIC, CaCu$_3$Ti$_4$O$_{12}$, SUBSTITUTED WITH Sr OR Ba

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January 2007

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

Faculty : Science

There has been a considerable interest in non-ferroelectric perovskite oxide CaCu$_3$Ti$_4$O$_{12}$ (CCTO). This material was discovered to possess one of the largest static dielectric constants, reaching nearly $\varepsilon \approx 80,000$ 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 CaCu$_3$Ti$_4$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 Ca$_{1-x}$Ba$_x$Cu$_3$Ti$_4$O$_{12}$ and Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ where $x = 0.5, 0.52, 0.56$ and $0.6$ at various temperatures. The substitutions were based on ionic radius ($r_{Ca} < r_{Sr} < r_{Ba}$) and the dielectric studies of Ca$_{1-x}$M$_x$Cu$_3$Ti$_4$O$_{12}$ (where M = Sr, 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 CaCu$_3$Ti$_4$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 Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ was observed while for Ca$_{1-x}$Ba$_x$Cu$_3$Ti$_4$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 Ca$_{1-x}$Ba$_x$Cu$_3$Ti$_4$O$_{12}$ and Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$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 CaCu$_3$Ti$_4$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 CaCu$_3$Ti$_4$O$_{12}$. 
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SIFAT DIELEKTRIK BAGI BAHAN PEMALAR BERASASKAN SERAMIJK CaCu$_3$Ti$_4$O$_{12}$ 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 CaCu$_3$Ti$_4$O$_{12}$ (CCTO) telah mendapat minat yang sewajarnya. Bahan ini didapat berjaya menghasilkan nilai pemalar dielektrik statik terbesar, menghampiri $\varepsilon \sim 80,000$ untuk sampel kristal tunggal pada suhu bilik. Bahan ini mempunyai struktur simetrik pada suhu bilik dengan kumpulan kubik $Im\overline{3}$. Disebabkan penghasilan sifat pemalar dielektrik tinggi yang luar biasa ini, kajian terhadap struktur dan sifat dielektrik CaCu$_3$Ti$_4$O$_{12}$ 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$_x$Cu$_3$Ti$_4$O$_{12}$ dan Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ 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$_x$Cu$_3$Ti$_4$O$_{12}$ (M = Sr dan Ba) masih belum dilaporkan.
Terdapat dua kategori dalam kajian penyelidikan ini. Pertama, kaedah belaun 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 menunjukan bahawa parameter kekisi CaCu$_3$Ti$_4$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 Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ dan bagi Ca$_{1-x}$Ba$_x$Cu$_3$Ti$_4$O$_{12}$ adalah fasa pelbagai dan beberapa elemen tidak tulen di dalam bahan. Adalah jelas bahawa untuk mengekalkan keseragaman molekul pada tindakbalas kimia Ca$_{1-x}$M$_x$Cu$_3$Ti$_4$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 padaan 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 Ca$_{1-x}$Ba$_x$Cu$_3$Ti$_4$O$_{12}$ dan Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$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 \(~ 2.6 \times 10^2\) 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 Fadhлина Bt. Che Ros on her Master Science thesis entitled “Dielectric Properties of High Dielectric Constant Ceramic CaCu$_3$Ti$_4$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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Date: 10 MAY 2007
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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