UNIVERSITI PUTRA MALAYSIA

STRUCTURAL ANALYSIS AND ELECTRICAL CHARACTERISATIONS OF Sr(1-x)CaxTiO3 AND Sr(1-x)BaxTiO3 CERAMICS

AZIZAH BINTI ISHAK

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STRUCTURAL ANALYSIS AND ELECTRICAL CHARACTERISATIONS OF $Sr_{(1-x)}Ca_xTiO_3$ AND $Sr_{(1-x)}Ba_xTiO_3$ CERAMICS

By

AZIZAH BINTI ISHAK

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

February 2008

DEDICATION

This dedication especially goes to my husband Samsudin Bin Mohd Said, my beloved parents Hj Ishak Shamsuddin and Hjh Yusti Isrin; my loving children Hazim, Haziq, Nabilah and Azfar; my brother Aziz, sisters Rozita, Rozana, Hanita and also to my mother-in-law Hjh Indon Shaari and all my dear friends.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

STRUCTURAL ANALYSIS AND ELECTRICAL CHARACTERISATIONS OF $Sr_{(1-x)}Ca_xTiO_3$ AND $Sr_{(1-x)}Ba_xTiO_3$ CERAMICS

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February 2008

Chairman : Associate Professor W. Mohamad Daud W. Yusof, PhD.

Faculty : Science

Ceramic samples of a structural formula $Sr_{1-x}Ca_xTiO_3$ (SCT) and $Sr_{1-x}Ba_xTiO_3$ (SBT) were prepared from the starting materials $CaCO_3$, $BaCO_3$, $SrCO_3$ and TiO_2 through the conventional solid state reaction technique. The XRD measurements reveals that the lattice parameter of $SrTiO_3$ changes after the substitution of Ba^{2+} and Ca^{2+} while the specimens, $Sr_{1-x}Ba_xTiO_3$ and $Sr_{1-x}Ba_xTiO_3$ showed the typical XRD patterns of perovskite polycrystalline structure without a preferred orientation; no second phase was observed.

The crystalline structure and dielectric properties of SCT and SBT ceramics with various compositions of *x* were investigated. The a- and c-axis lattice constants of SCT and SBT were calculated. It is found that the crystal structures of SBT are cubic phase when $x \leq 0.6$ and tetragonal phase when $x \geq 0.7$ at room temperature. However, the crystal structures of SCT is orthorhombic when $x \geq 0.1$ at room temperature.

The dielectric properties such as real permittivity or dielectric constant (ε'), imaginary permittivity or loss factor (ε'') and dielectric loss (tan δ) have been measured on the sintered disks with respect to frequency in the range 0.01 Hz to 1 GHz at room temperature and varying temperatures from 40^{o}C to 200^{o}C. Sample SBT-5 shows the largest value of the real permittivity($\varepsilon' = 4800$), low dielectric loss tangent (tan $\delta = 2.77$) and very low ac conductivity ($\sigma = 7.39\times10^{-9}$ S/cm) at 0.01 Hz.

Ceramic sample SCT shows very low dielectric conductivity,σ. The conductivity increases with frequency over the entire temperature range reflecting higher dielectric loss at higher temperature. In the impedance and modulus relaxation spectroscopy, the magnitude of imaginary impedance, Z'' maxima decrease with temperature indicating increasing loss in the resistive property of the sample. This behaviour of impedance pattern arises probably due to the presence of space charge in the material. The activation energy decreases from 0.301 eV to 0.221 eV when the composition of Ca^{2+} is increased from x = 0.3 to x = 0.9. The electric behavior of sample SBT showed that the activation energy has the value of 0.337 eV and 0.097 eV.

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

PENGANALISAAN STRUKTUR DAN PENCIRIAN ELEKTRIK BAGI SERAMIK $Sr_{(1-x)}Ca_xTiO_3$ DAN $Sr_{(1-x)}Ba_xTiO_3$

Oleh

AZIZAH BINTI ISHAK

Februari 2008

Pengerusi : Professor Madya W. Mohamad Daud W. Yusof, PhD.

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Sampel seramik yang mempunyai formula struktur $Sr_{1-x}Ca_xTiO_3$ (SCT) and $Sr_{1-x}Ba_xTiO_3$ (SBT) telah disediakan daripada bahan-bahan berikut iaitu $CaCO_3$, $BaCO_3$, $SrCO_3$ and TiO_2 menggunakan teknik konvensional tindakbalas keadaan pepejal. Pengukuran XRD menunjukkan parameter kekisi bagi $SrTiO_3$ berubah setelah didopkan dengan Ba^{2+} dan Ca^{2+}, manakala sampel $Sr_{1-x}Ba_xTiO_3$ dan $Sr_{1-x}Ba_xTiO_3$ menunjukkan corak spektrum yang biasa bagi struktur polikristilin perovskit di mana tiada perubahan orientasi; tiada fasa kedua.

Struktur kristal dan ciri-ciri dielektrik bagi sample seramik SCT dan SBT dengan komposisi *x* telah dikaji. Daripada pengiraan pemalar kekisi paksi-a dan paksi-c bagi sample SCT dan SBT, didapati struktur kristal bagi SBT adalah dalam fasa kiub apabila $x \leq 0.6$ dan fasa tetragonal apabila $x \geq 0.7$ pada suhu bilik. Manakala struktur kristal bagi SCT adalah ortorombik apabila $x \geq 0.1$ pada suhu bilik.

Sifat dielektrik seperti permittiviti nyata atau pemalar dielektrik (ε′), permittiviti maya atau faktor kehilangan (ε″) dan kehilangan dielektrik (tan δ) telah diukur ke atas disk yang telah disinter, terhadap frequensi di dalam renj 0.01 Hz ke 1 GHz pada suhu bilik dan juga perubahan suhu dari 40^{o}C ke 200^{o}C. Sampel SBT-5 mempunyai nilai nyata pemalar dielektrik yang maksimum ($\varepsilon' = 4800$), kehilangan tangent dielektrik yang rendah ($\tan \delta = 2.77$) dan nilai minima bagi kekonduksian ($\sigma = 7.39\times10^{-9}$ S/cm) pada 0.01 Hz.

Kekonduksian dielektri, σ, bagi sample seramik SCT menunjukkan nilai kekonduksian yang sangat rendah. Kekonduksian juga bertambah dengan frekuensi disepanjang renj suhu dan ini menunjukkan kehilangan dielektrik yang tinggi pada suhu yang tinggi. Dalam bahagian spektroskopi relaksasi bagi impedans dan modulus, magnitud bagi impedans khayalan Z″ maksima didapati berkurangan dengan suhu menunjukkan peningkatan dalam kehilangan sifat resistif pada sample tersebut. Perubahan pada corak impedans seperti ini adalah disebabkan oleh kewujudan cas ruang di dalam bahan. Didapati tenaga pengaktifan berkurangan dari 0.301 eV ke 0.221 eV apabila komposisi Ca^{2+} bertambah dari $x = 0.3$ ke $x = 0.9$. Ciri dielektrik bagi sampel SBT-1 menunjukkan tenaga pengaktifan mempunyai nilai 0.337 eV dan 0.097 eV.

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May Allah Bless You All!

I certify that an Examination Committee has met on 28 February 2008 to conduct the final examination of Azizah Binti Ishak on her Master of Science thesis entitled "Structural Analysis And Electrical Characterisations of $Sr_{1-x}Ca_xTiO_3$ and $Sr_{1-x}Ba_xTiO_3$ Ceramics" 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 degree of Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 14 August 2008

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.

AZIZAH BINTI ISHAK

Date : 20 August 2008

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LIST OF ABBREVIATIONS

ε	Dielectric permittivity
ε'	Real part of permittivity
ε''	Imaginary part of permittivity
ε_r	Relative dielectric permittivity
$\varepsilon(\omega)$	Dielectric permittivity as a function of angular frequency
σ	Conductivity
$\sigma(\omega)$	Conductivity as a function of angular frequency
τ	Relaxation time (sec)
ω	Angular frequency
ω_c	Critical angular frequency
ω_p	Peak angular frequency
ac	Alternating current
dc	Direct current
C*	Complex capacitance
C′	Real part of capacitance
C″	Imaginary part of capacitance
E	Activation energy
G	Conductance
M	Modulus
M*	Complex modulus
M′	Real part of modulus
M″	Imaginary part of modulus

MHz	Megahertz
R	Resistance
Y^*	Complex admittance
Y'	Real part of admittance
Y''	Imaginary part of admittance
Z^*	Complex impedance
Z'	Real part of impedance
Z''	Imaginary part of impedance
XRD	X-ray diffraction
SEM	Scanning electron microscope
EDX	Energy dispersive x-ray
Sr	Strontium
Ba	Barium
Ca	Calcium
ST	Strontium titanate
SBT	Strontium barium titanate
SCT	Strontium calcium titanate

CHAPTER 1

INTRODUCTION

A ceramic has traditionally been defined as "an inorganic, nonmetallic solid that is prepared from powdered materials, is fabricated into products through the application of heat, displays such characteristic properties as hardness, strength, low electrical conductivity and brittleness" (NDT, website). The word ceramic comes from Greek word "keramikos", which means "pottery." They are typically crystalline in nature and are compounds formed between metallic and nonmetallic elements.

The atoms in ceramic materials are held together by a chemical bond, The two most common chemical bonds for ceramic materials are covalent and ionic. Covalent and ionic bonds are much stronger than in metallic bonds and, generally speaking, this is why ceramics are brittle and metals are ductile. Many adopt crystalline structures, but some form glasses. The properties of the materials are a result of the bonding and structure.

Alkaline earth titanates of general formula $ATiO_3$ (A = Ca, Sr, Ba and Pb) and having perovskite structure are useful materials because of their wide applications in the electroceramics industry. Owing to their ferroelectric and piesoelectic properties, $BaTiO_3$ and $PbTiO_3$ form the basis of a veriety of electronic devices (Parkash et. al., 2003). Besides its relevance for electronics, sensor science, electrochemistry and photochemistry, $SrTiO_3$ (strontium titanate) is an excellent model material for a mixed type conductor because of availability of a detailed knowledge ot its defect models, chemical and transport parameters. Strontium tianate ($SrTiO_3$) is an incipient ferroelectric (or quantum paraelectric) in which a ferroelectric phase can be induced at a low temperature by isotrophic substitution or substitutional impurities as well as by external stress (Ping et al., 2008).

Perovskite materials with high dielectric permittivity have many applications in dyamic random access memories and ferroelectric non-volatile memories. High-K dielectric materials with low dielectric lossess are rewuired today for various applications in low dimention devices for a large frequency range, including optical domain (Barberacu et. al., 2008). The permittivity control of theses materials by a suitable DC bias field ensures a great opportunity of the phase control of the microwave devices. In this view strontium barium titanate (SBT), bulk ceramics and/or thin films in paraelectric state, is one of the promising material. Solid solution oxides of calcium strontium titante (SCT) with high dielectric constant and dielectric properties of a small temperature coefficient have attracted a great deal of attention for practical use as capacitor dielectrics (Ping et. al., 2008).

Electroceramics are advanced materials whose properties and applications depend on the close control of structure, composition, ceramic mixture, dopants and dopant (or defect) distribution (Irvine et. al.,1990). In the late 1980s, conventional processing methods for producing electroceramic materials (powder compacting, tape casting followed by sintering processes) were increasingly supplemented by thin film deposition techniques. Their properties can be tailored to operation as insulators, ferroelectric materials, highly conductive ceramics, electrodes as well as sensors and actuators.

1.1 Electronic Ceramics

Advanced materials and particularly advanced ceramics play an important role in the future of the world economy. The development and use of advanced ceramics are revolutionizing the field of material science and technology. Advanced ceramics are inorganic, nonmetallic materials with combinations of fine-scale microstructures, purity, complex compositions and crystal structures, and accurately controlled additives. Advanced ceramics can be classified into two groups, structural and electronic ceramics. The study of electronic ceramics involves many disciplines including chemistry, physics, metallurgy, mechanical engineering and material science.

Electronic ceramics can be divided into two main groups :

(i) insulators (dielectrics) and semiconductors, and

(ii) conductors (ionic and mixed).

The use of ceramics in electronics is becoming increasingly popular. Insulating ceramics are used extensively in consumer and industrial electronic system. Dielectrics are employed as capacitors to store charge and control the flow of current; for miniaturization of devices the ceramic layers should be as thin as possible. Special low loss dielectrics, operating as resonators are the key to the operation of mobile telephone handsets and base stations. Semiconducting ceramics (non-linear resistors) are employed as protection devices against power surges in almost all electronic and electrical system from computers to power distribution networks. Ceramic superconductors allow the flow of electricity with little or no resistance or heat loss. This gives the potential for trains floating on a magnetic cushion of air running at two to three hundred miles per hour and super computers the size of desktop calculators performing calculations thousands of times faster than any computer today.

The applications of ceramics in the electronics industry can be divided into two groups:

(i) the use of materials for interconnection and packaging of semiconductor circuits, and

(ii) the use of ceramics in circuit components which perform a function in their own right, such as capacitors and sensors (Whatmore , 1988).

The former application forms a large market and has been well reviewed elsewhere. The latter is particularly interesting because the materials which are used for a wide range of applications are in many cases closely related in crystal structure.

In many circuit functions, the material is required to give an electrical response to some stimulus. This can be as simple as giving a large change in induced electrical displacement for a small applied electric field, (i.e. having a large dielectric constant) if the material is for use as a capacitor dielectric.

Dielectric science has been a long-standing branch of physics, with close links to chemistry and electrical engineering. Over 130 years ago, Faraday coined the term “dielectric” to suggest that something analogous to current flow occurs through a capacitor structure during the charging process when current introduced at one plate “flows” through the insulator to charge the other plate. It is generally accepted that a dielectric material interacts with an electric field differently than does free space because the dielectric contain charges that can be displaced. Because all materials contain charges, essentially every material can be classified as a dielectric .

Dielectric ceramics can be divided into four categories according to their properties:

(i) high permittivity dielectric, ranging between 1000 to 25000, example $SrTiO_3$ and $BaTiO_3$.

(ii) medium permittivity dielectric, ranging between 50 to 200, example $CaTiO_3$.

(iii) low permittivity dielectric, ranging between 4 to 50, example $MgTiO_3$.

(iv) ultra-low permittivity dielectric, below 3, example SiO_2, and organic polymer (i.e. Teflon ® AF, parylene).

Based on the current technology and the increasing use of portable electronics the need to reduce the capacitance of electronic devices so that higher, less crosstalk and lower power consumption can be achieved using a very low permittivity insulator material. Meanwhile, high permittivity dielectrics have important applications in microelectronics and microwave communication system (Cho *et al*., 1995).

Good ceramic insulators should have relative dielectric constant or relative permittivity $\varepsilon < 30$, electrical resistivity $\rho > 10^{12}$ Ω cm, loss factor, tan $\delta < 0.001$, and consequently dielectric strength > 5 kV mm^{-1}. The review of dielectric properties of some ceramics is presented in Table 1.1.

Table 1.1 : Electrical property constants of different ceramic materials (Herbert, 1985).

Material	Dielectric constant at 1 MHz	Dielectric strength (kV/cm)
Air	1.00059	30
Polystyrene	2.54 - 2.56	240
Glass (Pyrex)	5.6	142
Alumina	4.5 - 8.4	16 - 63
Porcelain	6.0 - 8.0	16 - 157
Titanium dioxide	14 - 110	39 - 83

The trend in research of dielectric materials is to develop more low-dielectric constant materials for tomorrow integrated circuitary, The benefit to microelectronic devices are: higher speed, smaller size, higher frequency and lower operational power requirement.

1.2 Scope of Study

The ceramics form of $Sr_{1-x}Ca_xTiO_3$ (SCT) and $Sr_{1-x}Ba_xTiO_3$ (SBT) are of commercial importance as a ceramic capacitor dielectric and it is of scientific interest since it provides a straightforward example of the effect of solid solution composition of ceramics on dielectric properties. In this study, strontium titanate (ST) powders doped with Ca- and Ba- ions, are conventionally prepared by solid-state synthesis with different compositions and at very high temperatures, 1200^{o}C to 1350^{o}C.

SCT and SBT powders prepared by this method consist of non-uniform, submicrometer-sized coarse particle. The control of particle size distribution is not