UNIVERSITI PUTRA MALAYSIA

DIELECTRIC PROPERTIES OF STRONTIUM TITANATE AND CALCIUM TITANATE PREPARED VIA SOLID STATE AND MECHANICAL ALLOYING METHODS

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DIELECTRIC PROPERTIES OF STRONTIUM TITANATE AND CALCIUM TITANATE PREPARED VIA SOLID STATE AND MECHANICAL ALLOYING METHODS

By

WONG YICK JENG

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

April 2013

SPECIALLY DEDICATED TO

- My kind and helpful supervisor and co-supervisor, Associate Professor Dr. Jumiah Hassan and Associate Professor Dr. Mansor Hashim
- My beloved family for their endless support and encouragement
- My seniors and all my friends for their advice and assistance

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

DIELECTRIC PROPERTIES OF STRONTIUM TITANATE AND CALCIUM TITANATE PREPARED VIA SOLID STATE AND MECHANICAL ALLOYING METHODS

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Chairman: Jumiah Hassan, PhD

Faculty: Science

In this thesis, the phase formation, microstructure, and dielectric properties of strontium titanate ($SrTiO_3$) and calcium titanate ($CaTiO_3$) were investigated. Both samples were prepared using two different techniques, one by solid state reaction technique with the sintering temperature from 1200 to 1400°C at 40°C interval, and another by mechanical alloying method with the sintering temperature from 1000 to 1200°C at 40°C interval. From x-ray diffraction (XRD) analysis at room temperature, a single phase cubic $SrTiO_3$ structure with space group *Pm-3m* and a single phase orthorhombic $CaTiO_3$ structure with space group *Pnma* were obtained at 1200°C and above as both samples were prepared by solid state method. For the $SrTiO_3$ samples prepared by mechanical alloying method, the formation of a single phase cubic $SrTiO_3$ structure with space group *Pm-3m* could be achieved at 1160°C and above; whilst, a single phase orthorhombic $CaTiO_3$ with space group *Pnm*a could be formed starting from 1120°C and above. In all the synthesized samples, the morphological

analysis revealed that the grains were in submicron range with the calculated average grain sizes increased with sintering temperature.

The real part of relative permittivity ε_r', imaginary part of relative permittivity ε_r", and loss tangent tan δ have been measured on the sintered samples with respect to frequency range 0.01 Hz-1 MHz and varying temperatures from 25 to 250°C at 25°C interval. Meanwhile, the microwave dielectric measurements in the frequency range 1 MHz-1.5 GHz were also performed at room temperature. In the dielectric analysis at low frequency, ε_r' decreased with increasing frequency for both samples prepared by solid state and mechanical alloying methods. The values of ε_r' and tan δ showed an increase with the rise in temperature. The loss of all the samples under study at different measured temperatures were characterized by the loss peaks at particular frequencies. It indicated the presence of conductivity relaxation in the material. In the microwave frequency range, ε_r' remained constant for the $SrTiO_3$ and $CaTiO_3$ prepared by both methods, notably in the frequency range 10^7-10^8 Hz, whereas the values of ε_r" were relatively small which lied in the order of 10^{-2} in the same frequency range. At 1200°C, the room temperature values of ε_r' at 1 and 10 MHz of solid state prepared $SrTiO_3$ sample were about 27.7 and 43.6 respectively, while the room temperature values of ε_r' of mechanical alloyed $SrTiO_3$ samples were about 58.8 and 65.7 respectively. The room temperature values of ε_r' at 1 and 10 MHz for the solid state prepared $CaTiO_3$ samples sintered at 1200°C were about 19.4 and 42.4 respectively, while were about 132 and 205 respectively for the mechanical alloyed $CaTiO_3$ samples.

For all the investigated samples, ε_r' values increased with increasing sintering temperature in the low and microwave frequency range due to the grain growth with

respect to increasing sintering temperature. The grain growth rate of mechanical alloyed samples was larger than that of solid state prepared samples. Hence, the values of ε_r' were found to be enhanced in the samples prepared by mechanical alloying method. It was thus concluded that mechanical alloying processing route was thus a good alternative and yielded materials with improved dielectric properties if compared to that solid state method.

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

SIFAT DIELEKTRIK BAGI STRONTIUM TITANAT DAN KALSIUM TITANAT DISEDIAKAN MELALUI KAEDAH PEMPROSESAN SERAMIK DAN PENGALOIAN MEKANIKAL

Oleh

WONG YICK JENG

April 2013

Pengerusi: Jumiah Hassan, PhD

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Dalam tesis ini, pembentukan fasa, mikrostruktur, dan sifat dielektrik bagi strontium titanat ($SrTiO_3$) dan kalsium titanat ($CaTiO_3$) telah dikaji. Kedua-dua sampel telah disediakan dengan menggunakan dua teknik yang berlainan, satu melalui teknik pemprosesan seramik disinter dari suhu penyepuhlindapan 1200 ke 1400°C dengan selang 40°C, dan satu lagi disediakan melalui cara pengaloian mekanikal disinter dari suhu penyepuhlindapan 1000 ke 1200°C dengan selang 40°C. Dari analisis XRD pada suhu bilik, fasa tunggal bagi struktur kubus $SrTiO_3$ dengan kumpulan ruang *Pm-3m* dan fasa tunggal bagi struktur ortorombus $CaTiO_3$ dengan kumpulan ruang *Pnma* telah didapati pada suhu 1200°C ke atas bagi kedua-dua sampel yang disediakan dengan menggunakan pemprosesan seramik. Bagi sampel $SrTiO_3$ yang disediakan dengan menggunakan cara pengaloian mekanikal, pembentukan fasa tunggal bagi struktur kubus $SrTiO_3$ dengan kumpulan ruang *Pm-3m* boleh dicapai pada suhu 1160°C ke atas, manakala fasa tunggal bagi struktur ortorombus $CaTiO_3$ dengan kumpulan ruang *Pnma* boleh dibentuk bermula dari suhu 1120°C ke atas.

Dalam semua sampel tersinter, analisis morfologi mendedahkan butiran adalah dalam rantau submikron dengan purata saiz bijian menunjukkan peningkatan terhadap suhu penyepuhlindapan.

Ketelusan nyata relatif ε_r', ketelusan khayalan relatif ε_r", dan tangen kehilangan tan δ telah diukur terhadap sampel yang telah disinter dari frekuensi 0.01 Hz ke 1 MHz dan juga berubah terhadap pemanasan suhu dari 25 ke 250°C dengan selang 25°C. Sementara itu, frekuensi mikrogelombang dari 1 MHz ke 1.5 GHz juga dijalankan pada suhu bilik. Dari analisis dielektrik pada frekuensi rendah, ε_r' menurun dengan peningkatan frekuensi bagi kedua-dua sampel yang disediakan menggunakan pemprosesan seramik dan cara pengaloian mekanikal. Nilai untuk ε_r' dan tan δ menunjukkan peningkatan dengan peningkatan dalam pemanasan suhu. Kehilangan dielektrik bagi semua sampel yang dikaji pada pelbagai pemanasan suhu dicirikan oleh puncak tan δ pada frekuensi yang tertentu. Ini menandakan kewujudan santaian keberaliran dalam sampel. Dalam frekuensi mikrogelombang, ε_r' adalah malar bagi $SrTiO_3$ dan $CaTiO_3$ sampel yang disediakan menggunakan kedua-dua teknik, terutama dari frekuensi 10^7 ke 10^8 Hz, manakala nilai bagi ε_r" adalah agak kecil di mana ε_r" berkumpul di aras 10^{-2} di antara frekuensi yang sama. Pada suhu 1200°C, nilai untuk ε_r' yang diukur pada 1 dan 10 MHz di suhu bilik bagi $SrTiO_3$ yang disediakan menggunakan pemprosesan seramik ialah 27.7 dan 43.6 masing-masing, manakala untuk ε_r' bagi $SrTiO_3$ yang disediakan menggunakan cara pengaloian mekanikal pada suhu bilik ialah 58.8 dan 65.7 masing-masing. Nilai untuk ε_r' yang diukur pada 1 dan 10 MHz di suhu bilik bagi $CaTiO_3$ yang disediakan menggunakan pemprosesan seramik ialah 19.4 dan 42.4 masing-masing, manakala nilai-nilai untuk ε_r' bagi $CaTiO_3$ yang disediakan menggunakan cara pengaloian mekanikal pada suhu bilik ialah 132 dan 205 masing-masing.

Bagi semua sampel yang dikaji, nilai bagi ε_r' meningkat dengan peningkatan suhu penyepuhlindapan pada frekuensi rendah dan frekuensi mikrogelombang disebabkan penumbuhan butiran terhadap peningkatan suhu penyepuhlindapan. Kadar penumbuhan butiran bagi sampel yang disediakan menggunakan cara pengaloian mekanikal adalah besar berbanding dengan sampel yang disediakan melalui pemprosesan seramik. Oleh itu, nilai bagi ε_r' didapati meningkat bagi sampel yang disediakan melalui cara pengaloian mekanikal. Maka ini menyimpulkan bahawa teknik pengaloian mekanikal ialah alternatif yang bagus dan menghasilkan bahan-bahan dengan sifat dielektrik yang meningkat jika dibandingkan dengan pemprosesan seramik.

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I certify that a Thesis Examination Committee has met on 25 April 2013 to conduct the final examination of Wong Yick Jeng on his thesis entitled "Dielectric Properties of Strontium Titanate and Calcium Titanate Prepared via Solid State and Mechanical Alloying Methods" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student 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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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

WONG YICK JENG

Date: 25 April 2013

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