EFFECTS OF SINTERING TEMPERATURE ON MICROSTRUCTURE AND COMPLEX PERMITTIVITY OF MAGNESIUM TITANATE-DOPED BARIUM STRONTIUM TITANATE PREPARED VIA MECHANICAL ALLOYING

DAYANG NUR FAZLIANA BT ABDUL HALIM

ITMA 2018 25
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DAYANG NUR FAZLIANA BT ABDUL HALIM

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

December 2018
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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By

DAYANG NUR FAZLIANA BINTI ABDUL HALIM

December 2018

Chairman : Jumiah Hassan, PhD
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Uncovering the relationship between microstructure and dielectric properties is beneficial knowledge for finding high dielectric constant materials with low loss for technological purposes. Thus this research work attempts to understand the evolving relationship over sintering temperature between permittivity and microstructure properties in barium strontium titanate (BST), magnesium titanate (MT) and magnesium titanate doped barium strontium titanate (BST-MT). BST, MT and BST-MT samples were mechanically crush activated using a high energy ball mill for 10, 12 and 2 hours respectively. Pellets were formed followed by a sintering process from 500 °C up to 1300 °C with 100 °C increment. The phase analysis carried out using X-ray diffraction (XRD) showed a highly crystalline BST, MT or BST-MT ceramic could not be formed during milling alone. At 500 °C, the major reflection (Ba_{0.5}Sr_{0.5}TiO_3, MgTiO_3 or Ba_{0.5}Sr_{0.5}TiO_3/MgTiO_3) grew from a broad peak into a sharp peak as it reached 1300 °C. In BST-MT system, there was no trace of dopant, MgTiO_3 observed in XRD for all sintering temperatures. However, the energy dispersive X-ray (EDX) images confirmed the presence of Mg ion in BST-MT system. Sintering activity showed an improvement in the density where it increased from 3.67 g/cm^3 to 4.88 g/cm^3 for BST samples, 3.08 g/cm^3 to 3.56 g/cm^3 for MT samples and from 3.914 g/cm^3 to 5.318 g/cm^3 BST-MT sample. Field emission scanning electron microscope (FESEM) presented the average starting particle sizes were 39 nm, 89 nm and 78 nm for BST, MT and BST-MT respectively. There were an improvement in the grain growth where the grain size increased from 32.9 nm to 174.8 nm for BST, 87.5 nm to 1575.0 nm for MT and 80.8 nm to 267.5 nm for BST-MT. The dielectric properties investigated using the Agilent 4294A Impedance analyzer revealed the dielectric constant, \( \varepsilon'_r \) showed a decreasing trend below 10^4 Hz with increasing frequency for all samples due to the interfacial polarization. At 1 MHz, \( \varepsilon'_r \) increased from 49.28 to 143.68 (BST), from 28.15 to 47.39 (MT) and from 46.52 to 120.81 (BST-MT) with the rise of sintering temperatures. Therefore it revealed the dependency of dipolar polarization on the grain size and the...
crystalline structure resulting in a remarkable increase in polarizability. The tangent loss was found to decrease with frequency where a high tan δ at low frequency due to the decrement of hopping process of ions. The Nyquist plot in all sample revealed the attribution to the grain property of the material with the rise of sintering temperature. Complex modulus revealed one semicircle observed for higher sintered BST and MT. However, the introduction of dopant caused two semicircle observed for BST-MT sintered at 1200 °C and 1300 °C at all measuring temperatures suggesting the presence of both the grain and grain boundary contribution in the sample. BST-MT samples sintered at 1200 °C showed a prominent candidate for energy storage application as it experience a good physical properties with dielectric constant of 97.9 and 65% lesser dielectric loss compared to pure BST.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

KESAN SUHU SINTER KE ATAS STRUKTUR MIKRO DAN KETELUSAN KOMPLEKS UNTUK MAGNESIUM TITANAT-DIDOPKAN KEPADA BARIUM STRONTIUM TITANAT DISEDIAKAN MELALUI KAEDAH PENGALOIAN MEKANIKAL

Oleh

DAYANG NUR FAZLIANA BINTI ABDUL HALIM

Disember 2018

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Membongkar hubungan di antara struktur mikro dan sifat dielektrik adalah pengetahuan yang bermanfaat untuk mencari bahan dielektrik dengan pemalar yang tinggi dan kehilangan yang rendah untuk tujuan teknologi. Oleh itu, kerja-kerja penyelidikan ini cuba memahami hubungan terhadap suhu persinteran di antara sifat ketelusan dan struktur mikro di dalam barium strontium titanat (BST), magnesium titanat (MT) dan magnesium titanat didopkan kepada barium strontium titanate (BST-MT). Sampel BST, MT dan BST-MT secara mekanikal dihancurkan dengan mesin pengisar bola bertenaga tinggi masing-masing selama 10, 12 dan 2 jam. Pelet dibentuk diikuti dengan proses persinteran dari 500 °C hingga 1300 °C dengan kenaikan 100 °C. Analisis fasa yang dijalankan menggunakan pembelauan sinar-X (XRD) menunjukkan seramik BST, MT atau BST-MT yang berhablur tidak boleh dibentuk melalui proses pengisaran sahaja. Pada 500 °C, refleksi utama (Ba_{0.5}Sr_{0.5}TiO_3, MgTiO_3 atau Ba_{0.5}Sr_{0.5}TiO_3/ MgTiO_3) meningkat dari puncak yang luas ke puncak yang tajam apabila mencapai suhu 1300 °C. Di dalam sistem BST-MT, tiada kesan dopan, MgTiO_3 diperhatikan untuk semua suhu persinteran melalui XRD. Walau bagaimanapun, imej sinar-X tenaga serakan (EDX) mengesahkan kehadiran Mg ion dalam sistem BST-MT. Aktiviti persinteran menunjukkan peningkatan ketumpatan di mana ia meningkat daripada 3.67 g/cm^3 menjadi 4.88 g/cm^3 untuk sampel BST, daripada 3.08 g/cm^3 kepada 3.56 g/cm^3 untuk sampel MT dan daripada 3.914 g/cm^3 sehingga 5.318 g/cm^3 untuk sampel BST-MT. Mikroskop elektron pengimbaban pancaran medan (FESEM) mendedahkan purata saiz zarah permulaan ialah 39 nm, 89 nm dan 78 nm masing-masing untuk BST, MT dan BST-MT. Terdapat peningkatan di dalam pertumbuhan butiran di mana saiz butiran meningkat...
Sifat dielektrik yang dikaji menggunakan penganalisa rintangan Agilent 4294A menunjukkan pemalar dielektrik, $\varepsilon'$ menurun dengan peningkatan frekuensi di bawah $10^4$ Hz untuk semua sampel disebabkan oleh pengutuban di antara muka. Pada 1 MHz, $\varepsilon'$ meningkat dari 49.28 kepada 143.68 (BST), dari 28.15 kepada 47.39 (MT) dan dari 46.52 kepada 120.81 (BST-MT) dengan peningkatan suhu persinteran. Oleh itu ia mendedahkan pergantungan pengutuban dwikutub pada saiz butiran dan struktur hablur yang mengakibatkan peningkatan yang luar biasa di dalam pengutuban. Kehilangan tangen didapat berkurangan dengan frekuensi di mana nilai tan $\delta$ yang tinggi pada frekuensi rendah disebabkan oleh pengurangan proses melompat ion. Plot Nyquist di dalam semua sampel mendedahkan kehadiran sifat butiran bahan dengan peningkatan suhu persinteran. Modulus kompleks menunjukkan separuh bulatan diperhatikan untuk BST dan MT yang disinter pada suhu yang lebih tinggi. Walau bagaimanapun, pengenalan dopan menyebabkan dua separuh bulatan diperhatikan untuk BST-MT yang disinter pada 1200 °C dan 1300 °C untuk semua suhu pengukuran dan ini menunjukkan kehadiran sifat butiran dan butiran sempadan di dalam sampel. Sampel BST-MT yang disinter pada 1200 °C menunjukkan calon yang sesuai untuk aplikasi penyimpanan tenaga kerana ia mengalami sifat fizikal yang baik dengan pemalar dielektrik 97,9 dan 65% kadar kehilangan dielektrik yang lebih kecil berbanding dengan BST tulen.
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I certify that a Thesis Examination Committee has met on 28 December 2018 to conduct the final examination of Dayang Nur Fazliana binti Abdul Halim on her thesis entitled "Effects of Sintering Temperature on Microstructure and Complex Permittivity of Magnesium Titanate-Doped Barium Strontium Titanate Prepared via Mechanical Alloying" 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 Doctor of Philosophy.

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

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LIST OF ABBREVIATIONS

MgTiO$_3$  Magnesium titanate
Ba$_{0.5}$Sr$_{0.5}$TiO$_3$  Barium strontium titanate
BST  Barium strontium titanate
BST-MT  Magnesium titanate doped barium strontium titanate
MT  Magnesium titanate
$M^*$  Complex Modulus
$Z^*$  Complex Impedance
$\varepsilon'$  Dielectric Constant
$tan \, \delta$  Tangent loss
$T_c$  Curie temperature
$Z'$  Real part of impedance
$Z''$  Imaginary part of impedance
$M'$  Real part of modulus
$M''$  Imaginary part of modulus
$D$  Grain size of the sample
$T$  Absolute temperature
$Q$  Activation Energy
TEM  Transmission Electron Microscopy
XRD  X-ray Diffraction
FESEM  Field Emission Electron Microscopy
$\Omega$  Ohm
BPR  Ball to powder weight ratio
EDX  Energy Dispersive X-ray Spectroscopy
$\rho$  Density
$K$  Specific reaction rate
$\rho_{xrd}$  X-ray density
$P_{exp}$  Experimental density
$R$  Universal gas constant
CHAPTER 1

INTRODUCTION

1.1   Background of the Study

The development in ceramic materials started at the beginning of the 20th century with the advent of electronic in the radio and television broadcasts and the invention of transistor. Later, artificially synthesized raw materials and metallization and other technologies were developed to permit stronger ceramic-to-metal bonding, thus grew closer to today’s fine ceramic. Fine ceramics were made by scientifically controlling chemical compositions and manipulation of preparation methods to bring the realization of new materials customized to the unlimited amount of purpose they served. The variation in different conductivities is one of the greatest advantages of electronic ceramics since it can be designed to be conductors and insulators. Electronic ceramics can further be sub-divided into dielectric ceramics, magnetic ceramics, transparent ceramics, pyroelectric ceramics, semiconductive ceramics, and piezoelectric ceramics.

Many devices operate through the interaction of radio-frequency (RF) electromagnetic waves with electronic ceramic materials. There were great interest in characterization of the interface and interaction between fields and materials since it is a critical task in any electromagnetic (EM) device or instrument development, from nanoscale to larger scales (Kumar et al., 2009; Wang et al., 2004; Yoon et al., 2004). The electromagnetic interaction with electronic ceramic in radio-frequency region has unique properties such as the ability to travel in guided wave structures, the ability of antennas to launch waves that carry information over long distances, possess measurable phase and magnitude, the capability for imaging and memory storage, dielectric heating, and the ability to penetrate materials (Bakers-Jarvis and Kim, 2012). RF dielectrics are interesting materials which are friendly with electromagnetic waves. When it is irradiated with an electromagnetic wave, polarization is produced in these materials by alternative electric field at frequencies 3 kHz to 300 GHz wave. The RF dielectrics cause resonance which releases electromagnetic wave energy and vice versa.

Over the past thirty years, there is a fast growth in the technique of synthesizing the material in order to cope the industrial demand. Earlier, solid state reaction method is a very popular processing technique used to produce micron size material but with higher sintering temperatures (Sreedhar and Pavaskar, 2003). Nowadays, there are a lot of well-known
methods substantially modified with reduction in particle sizes such as sol gel technique (Ferreira and Baptista, 1994; Miao et al., 2006), water soluble single precursor method (Deng et al., 2010), and stearic acid gel routes (Li et al., 2010). Among the processes with the highest potential for tailoring advanced materials, mechanical alloying techniques are of special interest because they offer great flexibility in the choice of constituent materials to be combined, simplicity, and relatively inexpensive to produce (Koch et al., 1989). The effect of mechanical treatment is very huge as it can change the thermodynamic potential and reduce the sintering temperature by enhancing the atomic mobility thus stimulating different microstructural properties of material (Benjamin and Voilin, 1974). These properties do affect the dielectric performance of the materials as the dielectric properties are reliable on the microstructure where a homogenous sample with greater grain size and less pores will result in a good dielectric value. Thus, it is a critical step to choose an appropriate processing technique with a great constituent material to be combined in order to obtain desirable dielectric properties that fulfill technological requirements of developing market. In this research, barium strontium titanate (BST), magnesium titanate (MT) and a nanocomposite of barium strontium titanate and magnesium titanate (BST-MT) were chosen to be synthesized by mechanical alloying method aiming at developing nanostructured particles with low temperature properties and delivering better output than those produce via conventional technique.

1.2 Dielectric Materials

The discovery of the use of electrical insulation begins at the same age as the discovery of the electrical phenomena while the recognition of electrostatic appearances of electrification begins at an ancient age. A systematic investigation of dielectric properties may be traced in the 1870’s. Insulators are classified as materials used to prevent the flow of current by achieving lowest electrical conduction and maximum resistance while dielectric material is defined as insulators material which can be polarized by electric field (Jonscher, 1983).

The current tendency in dielectric materials based on TiO₂ is rising with a rapid development in capacitors, filters, mobile and satellite communication systems at higher frequencies. The development of new dielectrics especially the ferroelectrics, as well as the growth of the area of application of some of their special features have led to the creation of new types of dielectric devices for radio-electronic and optical equipment, and have induced large number of research in this field. For example, BaTiO₃ was the first material used for manufacturing dielectric ceramics capacitors, multilayer capacitors due to its high dielectric constant and low dielectric loss (Vijatovic et al., 2008). Later, BST (BaₓSr₁₋ₓTiO₃) which is derived from the prototype BaTiO₃ perovskite were discovered. With emerging properties
such as high power density, good reliability and highly nonlinear dielectric response to an applied electric field, BST became a leading candidate in dielectric storage (Ricketts et al., 2000).

Other than that, one of the promising materials is magnesium titanate, which has good dielectric properties such as intermediate dielectric constant, $\varepsilon' = 15-20$, low dielectric loss and high Q values; $Q = 20,000$ at 10 GHz (Belous et al., 2007). A number of researchers reported that the equilibrium phase of binary magnesium titanate showed existence of three stable phases $\text{MgTiO}_3$, $\text{Mg}_2\text{TiO}_4$ and $\text{MgTi}_2\text{O}_5$ (Filipovic et al., 2010 and Obrodovic et al., 2011). $\text{MgTiO}_3$ has the ilmenite structure; $\text{Mg}_2\text{TiO}_4$ has the spinel structure and $\text{MgTi}_2\text{O}_5$ has the pseudobrookite structure. Thus, magnesium titanate has attracted much attention in industrial applications such as multilayer capacitor, band-pass filters, oscillators in radar detectors, cellular telephones and global positioning satellite devices (Bernard and Houviet, 2004).

1.3 Problem Statement

Many reports were made generally on the influence of composition, effect of dopants and the relationship between the microstructure and dielectric properties of dielectric ceramic at higher sintering temperatures. For examples, Song et al., (2014) covered the effect of grain size on the energy storage of $\text{(Ba}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$ at 1260 $^\circ$C to 1400 $^\circ$C while Mohammadi and Fray (2012) studied the effect of different molar ratio of Mg:Ti on their microstructure properties. Extensive studies were also made for magnesium as a dopant effect on the BST ceramics as it will modify the dielectric permittivity (Ren et al., 2012; Zhang et al., 2009 and Xu et al., 2009).

However, the available literatures contain no sufficient data regarding the parallel evolution of microstructure and complex permittivity of the grain and grain boundaries of nanosize BST, MT and nanocomposite BST-MT relating them at lower temperatures until they are evolving towards their final form and values. There are several questions that become our most intention in this study such as what is the influence of microstructure-evolution changes on the dielectric properties at earlier and intermediate sintering condition? Secondly, how does the microstructure affect the dielectric permittivity in the frequency 40 Hz to 1 MHz? Hence, these findings will be the driving source of this research to build up new knowledge.
1.4 Objectives

The ultimate goal of this research is to track down the evolution studies between dielectric permittivity and their microstructure changes starting at lower sintering temperature (500 °C) up to its final state of form (1300 °C). This research attempted to understand the dielectric property-microstructure relationship in nanostructured polycrystalline of BST, MT and nanocomposite BST-MT in the frequency range 40 Hz to 1 MHz. The findings will be a good reference and guidance for the development of the new general theoretical model based on the evolution studies for both properties in the future. However, the necessary groundwork towards achieving the above goal has to be prepared in the form of detailed information on the materials response characteristics.

Hence, the work-step objectives for this research work are as follows;

1. To prepare and to characterize the phase formation and morphology studies of nanoparticles BST, MT and nanocomposite BST-MT via mechanical alloying.
2. To measure the complex permittivity of the as-prepared samples from 40 Hz to 1 MHz at different measuring temperatures starting from 30 °C up to 250 °C.
3. To correlate the microstructure and dielectric properties of the nanostructured samples sintered in a series of ascending temperatures.

1.5 Limitation of Study

Although the objectives in this thesis had been thoroughly investigated and studied, there are few limitations regarding to the research:

1. The dielectric measurement was carried out in the range of 40 Hz to 1 MHz
2. The composition of BST used in this research is Ba$_{0.5}$Sr$_{0.5}$TiO$_3$
3. The sintering temperature for all samples are in the range of 500 °C to 1300 °C.

1.6 Thesis Outline

This thesis comprises of six chapters. In the introduction, the dielectric material is briefly overview with an emphasis on dielectric application with respect to energy storage and cellular application. The research tools and expectations are stated. The second chapter deals with dielectric materials
viewed through the work by researchers in the last few decades. Several of the synthesis methods are also mentioned including the mechanical alloying method. The role of microstructure on the dielectric properties is also highlighted. The third chapter mentions the theory of polarization mechanisms, perovskite structure, fundamentals of dielectric permittivity and theory of mechanical alloying process. The fourth chapter states the experimental and measurement techniques which include the sample preparation and apparatus used for both dielectric permittivity and microstructure analysis. The parameters and physical measurements are defined. The fifth chapter presents the results of the relationship of microstructure and dielectric permittivity of nanostructured polycrystalline BST, MT and nanocomposite BST-MT. The final chapter summarizes the research findings and concludes some recommendations for further work.
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