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

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ITMA 2018 25

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By

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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

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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December 2018

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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 ^{o}C up to 1300 ^{o}C with 100 ^{o}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 ^{o}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 ^{o}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, ε_r' showed a decreasing trend below 10^4 HZ with increasing frequency for all samples due to the interfacial polarization. At 1 MHz, ε_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 ^{o}C and 1300 ^{o}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 ^{o}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

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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 ^oC hingga 1300 ^oC dengan kenaikan 100 ^oC. 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 ^oC, 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 ^oC. 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 pengimbasan 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

daripada 32.9 nm kepada 174.8 nm untuk BST, daripada 87.5 nm kepada 1575.0 nm untuk MT dan daripada 80.8 nm kepada 267.5 nm untuk BST-MT. Sifat dielektrik yang dikaji menggunakan penganalisa rintangan Agilent 4294A menunjukkan pemalar dielektrik, ε_r' menurun dengan peningkatan frekuensi di bawah 10^4 Hz untuk semua sampel disebabkan oleh pengutuban di antara muka. Pada 1 MHz, ε_r' 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 didapati berkurangan dengan frequensi di mana nilai tan δ 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 ^{o}C dan 1300 ^{o}C untuk semua suhu pengukuran dan ini menunjukkan kehadiran sifat butiran dan butiran sempadan di dalam sampel. Sampel BST-MT yang disinter pada 1200 ^{o}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.

ACKNOWLEDGEMENTS

I thank the Allah The Almighty for giving me the strength and patience to work through all these years. For all the encouragement and assistance along the way I am truly grateful. In particular I would like to acknowledge the following persons.

To my supervisor, Associate Professor Dr Jumiah Hassan, thank you for introducing me to the field and for outlining this research, your help and guidance along the way. I am deeply indebted my co-supervisor (late), Associate Professor Dr Mansor Hashim for his expert guidance and keen interest throughout the course of this study. I cherish his dedication in guiding me in my work despite of his ill health.

I would like to deeply thank the people who mean world to me, my parents, Hj Abdul Halim bin Said and Hjh Zainab binti Ismail and my mother in law Hjh Siti Rabiah binti Awang. I am especially grateful to my siblings for their unconditional trust, timely encouragement, endless patience and supporting me spiritually throughout my life.

I owe thanks to a very special person, my husband, Muhammad Shawal bin Husin for his continued and unfailing love, support and understanding during my pursuit of Ph.D that made the completion of thesis possible. You were always around at times I thought that it is impossible to continue, you helped me to keep things in focused. Much love for my kids Muhammad Suffy Dhrwisy and Muhammad Shafi Dayyan and this thesis dedicated to them.

Most importantly of all, I show extensive gratitude to my very best lab mates, Mutia Suhaibah Abdullah for always being there and bearing with me the good and bad times during my wonderful days of PhD. Without her willingness to share, the research would not have even been possible.

Collective thanks to the Institute of Advanced Technology and Department of Physics, UPM for providing me with the requisite institutional facilities throughout my research tenure. My heartfelt thanks to my fellow labmates, Mr Muhammad Aizat b Noor Ismail, Dr. Idza Riati Ibrahim, Dr. Shamsul Ezzad, Dr. Rodziah Nazlan, Dr. Nor Hapishah Abdullah, Dr. Wan Norailiana Wan Ab Rahman, Dr. Fadzidah Mohd Idris, Dr. Muhammad Syazwan Mustaffa, Dr. Alex See, Mr. Muhammad Misbah Muhamad Zulkimi, Mr. Ikhwan and Mr. Che Sulaiman Ahmad, who helped me by sharing their views and advice and by organising and participating in all the events.

I take this opportunity to sincerely acknowledge Ministry of Higher Education Malaysia for providing financial assistance through myBrain15 scholarship which supported me to pursue my research conveniently.

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
ε_r'	Dielectric Constant
tan δ	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
Ω	Ohm
BPR	Ball to powder weight ratio
EDX	Energy Dispersive X-ray Spectroscopy
ρ	Density
K	Specific reaction rate
ρ_{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 20^{th} 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 brings 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 TiO_2 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, $BaTiO_3$ 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 ($Ba_xSr_{1-x}TiO_3$) which is derived from the prototype BaT_iO_3 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, ε' = 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 $MgTiO_3$, Mg_2TiO_4 and $MgTi_2O_5$ (Filipovic et al., 2010 and Obrodovic et al., 2011). $MgTiO_3$ has the ilmenite structure; Mg_2TiO_4 has the spinel structure and $MgTi_2O_5$ 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 $(Ba_{0.4}Sr_{0.6})TiO_3$ at 1260 ^oC to 1400 ^oC 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 workby 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.

REFERENCES

Almond D. P., & West A. R. (1983). Impedance and modulus spectroscopy of “real” dispersive conductors.*Solid State Ionics*. 11(1), 57-64.

Arya P. R., Jha P., and Ganguli A. (2003). Synthesis, characterization and dielectric properties of nanometer-sized barium strontium titanate prepared by the polymeric citrate precursor method, *J. of Materials Chemistry*. 13, 415-423.

Bakers-Jarvis J. and Kim S. (2012). The Interaction of Radio-Frequency Fields With Dielectric Materials at Macroscopic to Mesoscopic Scales. *Journal of Research of the National Institute of Standards and Technology*. 17.

Barsoukov E. and Macdonald J. R. (2005). *Impedance Spectroscopy Theory, Experiment, and Applications*. Hoboken, New Jersey :Wiley.

Barik S. K., Choudhary R. N. P., and Singh A. K. (2011). AC impedance spectroscopy and conductivity studies of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramic. *Advanced Material Letters.* 2 (6), 419-424.

Bauerle J. E. (1969). Study of solid electrolyte polarization by a complex admittance method. *Journal of Physics and Chemistry of Solids*. 30, 2639-2798.

Belous A., Ovchar O., Durylin D., Valant M., Macek-Krzmanc M. and Suvorov D. (2007). Microwave composite dielectric based on magnesium titanates. *J. of the Eur. Ceram. Soc.* 27, 2963

Benjamin J.S. and Voilin T.E. (1974). The mechanism of MA. *Metall. Trans,* 5, 1929.

Bernard J., and Houviet D. (2004). $MgTiO_3$ for Cu base metal multilayer ceramic capacitors. *Jour. Eur. Ceram. Soc*. Vol 4, 1877-1881.

Bian Y. and Zhai J. (2014). Low dielectric loss $Ba_{0.6}Sr_{0.4}TiO_3/MgTiO_3$ composite thin film prepared by a sol gel process. *Journal of Physics and Chemistry of Solids*. 75, 759-764.

Chanda M. (1980). *Science of engineering materials*.Vol. 3, the Macmillan Company of India Ltd.

Cheng L., Liu P., Qu S-X., Cheng L. and Zhang H. (2014). Microwave dielectric properties of Mg_2TiO_4 ceramics synthesizedvia high energy ball milling method. *Journal of Alloys and Compound,*

Chou X., Zhai J. and Yao X. (2007). Dielectric tunable properties of low dielectric constant $Ba_{0.5}Sr_{0.5}TiO_3$-Mg_2TiO_4 microwave composite ceramic, *Applied Physics Letters*, 91, 122908.

Chou X., Zhao Z., Du M., Liu J. and Zhai J. (2012). Microstructures and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramic doped with B_2O_3-Li_2O Glasses for LTCC technology applications. *Journal Material Science*. 28, 280-284.

Coble R. L. (1961). Sintering crystalline solids. II. Experimental test of diffusion models in powder compact, *Journal Applied Physics,* 32, 793-799.

Cui J., Dong G., Yang Z. and Du, J. (2010). Low dielectric loss and enhanced tunable properties of Mn-doped BST/MgO composites. *Journal of Alloys and Compound*, 490, 353-357.

Das S., Das S. and Sutradhar S. (2017). Enhanced dielectric behavior and ac electrical response in Gd-Mn-ZnO nanoparticles. *Journal of Alloys and Compounds*, 726, 11-21.
Deng Y. F., Tang S. D., Lao L. Q. and Zhan S. Z. (2010). Synthesis of magnesium titanate nanocrystalline from a cheap and water soluble single precursor. Inorganica Chimica Acta, 363, 827-829.
Fathi M. and Zahrani E.M. (2009). The Effect of High-Energy Ball Milling Parameters on the Preparation and Characterization of Fluorapatite Nanocrystalline Powder. Ceramic International, 35(6):2311-2323
Ferreira V.M. and. Baptista J.L. (1994). Preparation and microwave dielectric properties of pure and doped magnesium titanate ceramics. *Materials Research Bulletin*, Vol 29, 1017.
Filipovic S., Obradovic N., Pavlovic, V.B., Markovic, S., Mitric, M. and Ristic, M.M. (2010). Influence of mechanical activation on microstructure and crystal structure of sintered $MgO-TiO_2$ system. *Sci. of Sintering*. 42, 143.
Filipovic S., Pavlovic V.P., Obradovic N., Paunovic V., Maca K. and Pavlovic V.B. (2017). The impedance analysis of sintered $MgTiO_3$ ceramics. *Journal of Alloys and Compounds*, 701, 107-115.
Frey M. H.,Xu Z., Han P. and Payne D. A. (1998). The role of interfaces on an apparent grain size effect on the dielectric properties for ferroelectric barium titanate ceramics, Ferroelectrics. 206:1, 337-353.
Gerhardt R. (1994). Impedance and dielectric spectroscopy revisited: distinguishing localized relaxation from long-range conductivity, *Journal of Physics and Chemistry of Solids*. 55(12), 1491-1506.
Goldman A. (1999). *Handbook of modern ferromagnetic materials*. Boston/Dordrecht/London.
Hamieh T.. Kawtharani F., Kassas A., Quercioli R., Houivet D., Bernard J., Lakiss H., Toufaily J., Aoun R. and Reda M. (2013). Ultrafine Grinding of $MgTiO_3$ Based Ceramic Influencing the Material Properties. *Journal of Physical Chemistry & J Biophysics*, 3 (3), 122-135.
Ioachim A., Banciu M. G. and Nedelcu L. (2005). Microwave dielectric properties of doped $Ba_{0.5}Sr_{0.5}TiO_3$ ceramics correlated with sintering temperature. *Journal of Optpelectronics and Advanced Materials*, 7, 3023-3027.
Izumskaya N., Alivov Y. and Morkoc H. (2010). *Oxides, oxides, and more oxides: high-k oxides, ferroelectrics, ferromagnetics, and multiferroics*. Critical Reviews in Solid State and Materials Sciences, Virginia Commonwealth University, Richmond.
Jacob R., Harikrishnan G. and Isac J. (2015). Impedance spectroscopy and dielectric studies of nanocrystalline iron doped barim strontium titanate ceramics. *Processing and Application of Ceramic*, 9 (2), 73-39.
Jonscher A. K. (1983). Dielectric relaxation in solids, *Chelsea, Dielectric Press,* London. 3, 231.
Joong S. and Kang L. (2005). *Sintering Densification, Grain Growth and Microstructure.* London: Elsevier/Butterworth-Heinemann.

Koch C. C., Cavin O. B., McCamey C. G., Scarborough J. O., (1983)., Preparation of ''amorphous'' $Ni_{60}Nb_{40}$ by mechanical alloying. *Appl. Phys. Lett.* (43): 1017- 1020.

Kosanović D., Živojinović J., Obradović N., Pavlović V.P., Pavlović V.B., Peleš A. and Ristić M.M. (2014). The influence of mechanical activation on the electrical properties of $Ba_{0.77}Sr_{0.23}TiO_3$ ceramics. *Ceramics International*, 40, 11883-11888.

Kumar P., Singh S., Juneja J. K., Prakash C. and Raina K.K. (2009). Ferroelectric properties of substituted barium titanate ceramics. *Physica B*. 404,1752-1756.

Kurchannia R., Bell A.J., Chakraborty T. and Hunter I.C. (2004). An investigation of BST:$MgTiO_3$ and X7R:$MgTiO_3$ Based Ceramics for Microwave Applications. *International Ultrasonics, Ferroelectrics and Frequency Control Jointh 50th Annivesary Conference*.281-284.

Li D., Wang L. and Xue D. (2010). Staeric acid gel derived MgTiO3 nanoparticles: A low temperature intermediate phase of Mg_2TiO_4. *Jour. Of Alloys and compound*,. 564.

Lu X., Tong Y., Zhang L., Ma B., Cheng, Z.-Y (2018). High dielectric tenability in composite prepared using SiO2 coated $Ba_{0.5}Sr_{0.5}TiO_3$ nanoparticles. *Ceramic International*. 44, 9875-9879.

Luo W., Guo J., Randall C. and Lanagan M. (2017). Effect of porosity and microstructure on the microwave dielectric properties of rutile. *Materials Letters*, 200,101–104

Ma P., J., Meng L., Li J., Ding L., Wang J. and Zhang H-W. (2009). Preparation and dielectric properties of BST-Mg_2TiO_4 composite ceramics. *Materials Chemistry and Physics.* 114,624-628.

Mahajan S., Haridas D, Ali S.T., Munirathnam N.R., Sreenivas K., Thakur O.P. and Prakash C. (2014). Investigation of conduction and relaxation phenomena in $BaZr_xTi_{1-x}O_3$ (x=0.05) by impedance spectroscopy. *Physica B*, 451, 114-119.

Mangalaraja R.V., Manohar P., Gnanam F.D. and Awano M. (2004). Electrical and magnetic properties of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite prepared by sol-gel method, *J. Material Science*. 39 2037.

Mao C., Yan S., Cao S., Yao C., Cao F., Wang G., Dong X., Hu X. and Yang C.(2014). Effect of grain size on phase transition, dielectric and pyroelectric properties of BST ceramics. J*ournal. of European Ceramic Society*. 34 2933-2939.

Melanie S. (2014). *Microstructure Evolution In Strontium Titanate: Investigated by means of grain growth simulations and x-ray diffraction contrast tomography experiments*. Karlsruher Institu fur Technology.

Miao Y-M., Zhang Q-L., Yang H. and Wang H-P. (2006). Low-temperature synthesis of nano-crystalline magnesium titanate materials by the sol-gel method. *Material Science and Engineering B*, 128, 103-106.

Mohammadi M.R. and Fray D. J. (2012). Tailoring of morphology and crystal structure of nanomaterials in MgO-TiO_2 system by controlling Mg:Ti molar ratio. *Journal Sol-Gel Science Technology*, 64, 135-144.

Morintale E., Scarisoreanu N., Dinescu M. and Rotaru P. (2010). Thermal stability of BST in a vast range of temperature. *Physics AUC*, 20, 83-89.

Moulson A.J and Herbert J.M (2003). *Electroceramics*: Materials, Properties, Applications. Second Edition, John Wiley & Sons Inc., England.

Obrodovic N., Filipovic S., Pavlovic V.B., Maricic A., Mitrovic N. and Ristic M.M. (2011). Sintering of mechanically activated magnesium-titanate and barium-zinc-titanate ceramics. *Sci. of Sintering*. 43, 145.

Ortega N., Kumar A., Bhattacharya P., Majumder, S. B. and Katiyar R. S. (2008). Impedance spectroscopy of multiferroic $PbZr_xTi_{1-x}O_3/CoFe_2O_4$ layered thin films. *Phys. Rev.B*. 77, 014111.

Ozdemir I., Ahrens S., Mucklich S., Bemhard W. (2008). Nanocrystalline Al_2O_3 and SiC composites produced by high energy ball milling. *Journal Material Process Technology,* 205, p. 111-118.

Patel N.D., Mangrola M.H., Soni G. K., and Joshi V.G. (2017). Structural and electrical properties of nanocrystalline barium strontium titanate, *Materials Today:* Proceeding 4, 3842-3851.

Pecnik T., Glinsek S., Kmet B. and Malic B. (2015). Combined effects of thickness, grain size and residual stress on the dielectric properties of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films, *Journal of Alloys and Compound*. 646, 766-772.

Petzelt J. (2010). Dielectric grain-size effect in high-permittivity ceramics,Ferroelectrics. 400:1, 117-134.

Pfaff G. (1994). Peroxide route for synthesis of magnesium titanate powders of various compositions. *Ceramics International,* 20, 111-116.

Raihan R., Rabbi F., Vadlamudi V. and Reifsnider K. 2015. Composite Materials Damage Modeling Based on Dielectric Properties. *Material Sciences and Applications*. Vol 6, 1033-1053.

Ram M. and Chakrabarti S. (2008). Dielectric and modulus behavior of $LiFe_{1/2}Ni_{1/2}VO_4$ ceramics. *Journal of Physics and Chemistry*, 69, 905-912.

Ranjan R., Kumar R., Kumar N., Behera B. and Choudhary R.N.P. (2011). Impedance and electric modulus analysis of Sm-modified $Pb(Zr_{0.55}Ti_{0.45})_{1-x/4}O_3$ ceramics. *Journal of Alloys and Compounds*, 509, 6388-6394.

Ren P., Fan H., Wang X. and Liu K. (2012). Effects of Magnesium Doping on the phase transitions and dielectric figure of merit of barium strontium titanate ceramics. *International journal of Applied Ceramic Technology*, 9, 358-365.

Ricketts, B.W., Triani, G. and Hilton, A.D. (2010). Dielectric energy storage densities in $Ba_{1-x}Sr_xTi_{1-y}Zr_yO_3$ ceramics. *Journal Material Science – Mater Electron*. 11, 513-517.

Rouahi A., Kahouli A., Sylvestre A., Defay E. and Yangui B. (2012). Impedance spectroscopic and dielectric analysis of Ba0.7Sr0.3TiO3 thin films. *Journal of Alloys and Compounds.* 529, 84-88.

Saif A. A. and Poopalan P. (2011). Correlation between the chemical composition and the conduction mechanism barium strontium titanate thin films,*J. of Alloys and Comp*. 509, 7210-7215.

Samyuktha V. S., Suvarna R. P. and Rao T. S. (2016). Synthesis and dielectric properties of $MgTiO_3$ ceramic material. *International Journal of Engineering Research and Technology*. 5, 245-249.

Shukla A., Choudhary R. and Thakur A. (2009). Thermal, structural and complex impedance analysis of Mn^{4+} modified $BaTiO_3$ electroceramic. *Journal Physics Chemical Solids*, 70 (11), 1401-1407.

Song Z., Liu H., Zhang S., Wang Z., Shi Y., Hao H., Cao M., Yao Z. and Yu, Z. (2014). Effect of grain size on the energy storage properties of $(Ba_{0.4}Sr_{0.6})TiO_3$ paraelectric ceramics, *Journal of the European Ceramic Society*. 34, 1209-1217.

Sreedhar K. and Pavaskar N. R. (2002). Synthesis of MgTiO3 and $Mg_4Nb_2O_9$ using stoichiometrically excess MgO, *Material Letters*, 53, 452-455.

Stubičar N., Tonejc A. and Stubicar, M. (2004).Microstructural Evolution of some $MgO-TiO_2$ and $MgO-Al_2O_3$ powder mixtures during high energy ball milling and post-annealing studied by X-ray diffraction. *J. Alloys and Compound*. 370, 296-301.

Su H., Zhang H., Tang X. and Jing Y. (2006). Effects of calcining temperature and heating rate on properties of high-permeability NiCuZn ferrites. *Journal of Magnetism and Magnetic Materials*, 302(2), 278-281.

Suryanarayana C. (2001). Mechanical alloying and milling. *Progress in Materials Science*, 46 (1-2), 1-184.

Suryanarayana C. (2004). *Mechanical alloying and milling*. New York: Marcel Dekker.

Suryanarayana C., and Koch C. C. (2000). Nanocrystalline materials – Current research and future directions. *Hyperfine Interact*. 130, 5.

Tayal D. C. (1988). Electricity and Magnetism, *Himalaya Publishers.* 5, p. 372.

Ulrich R., Schaper L., Nelms D. and Leftwich M. (2000). Comparison of Paraelectric and Ferroelectric Materials for Applications as Dielectrics in Thin Film Integrated Capacitors. *The International Journal of Microcircuits and Electronic Packaging,* Volume 23, Number 2

Vendik O.G. and Zubko S.P. (2000). Ferroelectric phase transition and maximum dielectric permittivity of displacement type ferroelectrics $(Ba_xSr_{1-x}TiO_3)$. *J Appl Phys,* 88(9), 5343-5350.

Vijatović M. M., Bobić J. D. and Stojanović B. D. (2008). History and Challenges of Barium Titanate: Part. *Science of Sintering,* 40, 235-244

Wakino K. (1989). Recent development of dielectric resonator materials and filters in Japan. *Journal Ferroelectrics.* 91, 69-86.

Wang X., Chen R., Zhou H., Li L. and Gui Z. (2004). Dielectric properties of $BaTiO_3$-based ceramic sintered in reducing atmospheres preparedfrom nano-powders. *Ceramic International*, 30, 1895-1898.

Wang X., Chen R., Zhou H., Li L. and Gui Z. (2004). Dielectric properties of $BaTiO_3$-based ceramic sintered in reducing atmospheres prepared from nano-powders. *Ceramic International*, 30, 1895-1898.

Wechsler B.A. and Navrotsky A. (1984). Thermodynamics and structural chemistry of compounds in the system $MgO-TiO_2$. *Journal of Solid State Chemistry*, 55, 165-180.

Widegren J. and Bergstrom L. (2002). Electrostatic stabilization of ultrafine titania in ethanol, *Journal American Ceramic Society,* 85, 523-528.

Wong Y.J., Hassan J. and Hashim M. (2013). Dielectric properties, impedance analysis and modulus behavior of $CaTiO_3$ ceramic prepared by solid state reaction. *Journal of Alloys and Compounds,* 571,138-144

Xu Q., Zhang X., Huang Y., Chen W., Liu H., Chen M. and Kim B. (2009). Effect of MgO on structure and nonlinear dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$/MgO composite ceramics prepared from superfine powders. *Journal of Alloys and Compounds*, 488, 448-453.

Yamaguchi O., Yamamoto S. and Shimizu K. (1981). Kinetics of formation of alkoxy-derived $MgO.2TiO_2$ and $MgO.TiO_2$. *Ceramics International*, 73-74.

Yoon D-H., Zhang J. and Lee B.I. (2003). Dielectric constant and mixing model of $BaTiO_3$ composite thick films. *Material Research Bulletin*, 38, 765-772.

Zhang H., O, S.W. and Chan H.L.W. (2009). Synthesis of fine-crystalline $Ba_{0.6}Sr_{0.4}TiO_3$-MgO ceramics by novel hybrid processing route. *Journal of Physics and Chemistry of Solids*, 70, 1218-1222.

Zhang J., Shen B., Zhai J. and Yao X. (2013). Microwave dielectric properties and low sintering temperature of $Ba_{0.5}Sr_{0.5}TiO_3$-Mg_2TiO_4 composites synthesized in situ by the hydrothermal method. *Ceramic International*, 39, 5943-5948.

Zhang L., Wu P., Li Y., Cheng Z.-Y. and Brewer J. C. (2014). Preparation process and dielectric properties of $Ba_{0.5}Sr_{0.5}TiO_3$–P(VDF–CTFE) nanocomposites.*Composite Part B : Engineering.* Vol 56, 284-289.

Zhang Q., Zhai J., Shen B., Zhang H. and Yao X. (2013). Grain size effects on dielectric properties of barium strontium titanate composite ceramics. *Materials Research Bulletin*, 48, 973-977.