UNIVERSITI PUTRA MALAYSIA

ELECTRICAL PROPERTIES OF MIXED OXIDES OF MANGANESE AND VANADIUM PREPARED BY CONVENTIONAL SOLID STATE AND MECHANICAL ALLOYING METHODS

TAN FOO KHOON

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By

TAN FOO KHOON

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement of the Degree of Doctor of Philosophy

June 2016

SPECIALLY DEDICATED TO

- My friendly and helpful supervisory committee, Assoc. Prof. Dr. Jumiah Hassan, the late Assoc. Prof. Mansor Hashim and Assoc. Prof. Zaidan Abdul Wahab.

- My beloved wife and family members for their moral support and encouragement.

- My seniors, lab mate and all my friends for their assistance.

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

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June 2016

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Metal oxide of manganese (Mn) and vanadium (V) are widely studied due to their interesting fundamental physical properties. There were several works on Mn-V mixed oxide done previously, but it still lacks comprehensive electrical studies on Mn-V oxide system which can gives more information to describe the mixed oxide. In this project, the investigation toward morphology, electrical conductivity, dielectric properties and thermal diffusivity of the mixed oxides was carried out. The samples were prepared by conventional solid state (SS) and mechanical alloying (MA) methods. The samples were prepared with a ratio of 40 mol% of V_2O_5 and 60 mol% of $2MnO_2$ and were sintered at different sintering temperatures from 500 to 800^oC and characterized. In the meantime, samples of pure oxides, Mn and V were also prepared to compare with the mixed oxides.

X-ray Diffraction confirmed that the samples prepared are multi phases and Rietveld refinement method was employed to estimate the phase composition in each sample. MA method successfully reduced the sintering temperature for the reaction to occur at a much lower temperature compare to SS method. Also, the surfaces of the sample were visualized using Field emission scanning electron microscopy (FESEM) and the average grain size was calculated. From FESEM images, MA method produced very fine particles in nano-scale while SS method in micro-scale.

The DC and AC conductivities of the samples showed the semiconducting behavior because the electrical conductivity increases when temperature increased. The Mn-V oxides have lower electrical conductivity as compare to the starting materials. Since the samples are multi phases, hence the dielectric constant obtained is a contribution from different phases. The polarization mechanism in this frequency region (40 to 1 MHz) can be explained by interfacial and dipolar polarization. On the other hand, the spectra of electric modulus and impedance of the samples successfully revealed the dielectric relaxation process which cannot be observed directly from dielectric loss spectrum. Equivalent circuit modeling was adopted to further describe and predict the electrical

properties of the material. The samples were successfully fitted to single parallel RC circuit or two parallel RC circuits connected in series.

The sample sintered at 500^{o}C prepared using MA method gave the best dielectric properties. This is possibly due to MA method reduces the particle size and increases the grain boundary volume of the sample. Also, the MA series have better thermal stability and gave higher thermal diffusivity compare to SS series where the heat from energy dissipation can be easily transferred for the cooling process.

Lastly, a more comprehensive electrical and thermal study on Mn-V oxide system is done and it can be a reference for future researchers.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SIFAT ELEKTRIK BAGI CAMPURAN OKSIDA DARI MANGAN DAN VANADIUM YANG DISEDIAKAN MELALUI KAEDAH PEMPROSESAN SERAMIK AND PENGALOIAN MEKANIKAL

Oleh

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Oksida logam mangan (Mn) dan vanadium (V) dikaji secara meluas atas sifat-sifat fizikal asasnya yang menarik. Terdapat beberapa kerja-kerja penyelidikan pada oksida campuran Mn-V dilakukan sebelum ini, tetapi ia masih tidak mempunyai sebuah kajian elektrik yang lengkap mengenai sistem oksida Mn-V yang boleh memberi maklumat lanjut untuk menggambarkan oksida campuran. Dalam projek ini, siasatan terhadap morfologi, kekonduksian elektrik, sifat dielektrik dan kemeresapan terma bagi oksida campuran telah dijalankan. Sampel telah disediakan dengan kaedah pemprosesan seramik (SS) dan pengaloian mekanik (MA). Sampel telah disediakan dengan nisbah 40 mol% daripada V_2O_5 dan 60 mol% daripada $2MnO_2$ dan telah disinter pada suhu suhu pensinteran yang berbeza dari 500 hingga 800 ^oC dan dicirikannya. Pada masa yang sama, sampel-sampel oksida tulen, Mn dan V juga disediakan untuk dibanding dengan oksida campuran.

X-ray Diffraction mengesahkan bahawa sampel yang disediakan adalah dalam pelbagai fasa dan kaedah penyempurnaan Rietveld telah digunakan untuk menganggarkan komposisi fasa dalam setiap sampel. Kaedah MA berjaya mengurangkan suhu pensinteran menyebabkan tindak balas yang berlaku adalah pada suhu yang lebih rendah berbanding dengan kaedah SS. Juga, permukaan sampel itu diperhatikan menggunakan medan imbasan mikroskop elektron (FESEM) dan saiz bijian purata dikira. Daripada imej FESEM, kaedah MA menghasilkan zarah yang sangat halus dalam skala-nano manakala kaedah SS dalam skala-mikro.

Kekonduksian DC dan AC bagi sampel-sampel menunjukkan sifat semikonduktor kerana peningkatan kekonduksian elektrik dengan peningkatan suhu. Oksida Mn-V mempunyai kekonduksian elektrik yang lebih rendah berbanding dengan bahan mentah. Oleh kerana sampel mempunyai pelbagai fasa, maka pemalar dielektrik yang diperolehi adalah dari sumbangan fasa-fasa yang berbeza. Mekanisme polarisasi di julat frekuensi ini (40-1 MHz) dapat dijelaskan oleh polarisasi antaramuka dan dwikutub. Selain itu, modulus elektrik dan impedans sampel berjaya mendedahkan

proses kesantaian dielektrik yang tidak dapat diperhatikan secara terus daripada spektrum faktor lesapan dielektrik. Pemodelan litar setara telah diggunakan supaya boleh menghurai dan meramalkan sifat-sifat elektrik bagi sesuatu bahan. Sampel-sampel telah berjaya diwakilkan ke satu litar RC selari atau dua litar RC selari disambung secara sesiri.

Sampel disinter pada suhu 500^{o}C disediakan dengan menggunakan kaedah MA mempunyai sifat dielektrik yang terbaik. Ini mungkin disebabkan oleh kaedah MA mengurangkan saiz zarah dan meningkatkan jumlah sempadan bijian dalam sampel. Juga, siri MA yang mempunyai kestabilan terma yang lebih baik dan memberikan kemeresapan terma yang lebih tinggi berbanding dengan siri SS maka haba dibebaskan dari pelesapan tenaga boleh meresap dengan mudah bagi proses penyejukan.

Akhir sekali, kajian elektrik dan haba yang lebih menyeluruh ke atas sistem oksida Mn-V dilakukan dan ia boleh menjadi rujukan kepada penyelidik akan datang.

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Finally, I wish to thank my heavenly parents, wife, siblings and my lovely friends for their moral and resources support. Also, thanks to everyone who directly or indirectly bring to the completion of my project.

I certify that a Thesis Examination Committee has met on 8 June 2016 to conduct the final examination of Tan Foo Khoon on his thesis entitled "Electrical Properties of Mixed Oxides of Manganese and Vanadium Prepared by Conventional 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 Doctor of Philosophy.

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LIST OF SYMBOLS

C	Capacitance
C_{gb}	Grain boundary capacitance
C_g	Grain capacitance
F	Farad
R	Resistance
R_{gb}	Grain boundary resistance
R_g	Grain resistance
Ω	Ohm
G	Conductance
f	Frequency
I	Current
E	Electric field
σ	Magnitude of surface charge density
Q	Magnitude of total charge
V	Potential difference
A	Area of each plate or cross-sectional area
d	Separation between the plates
C_o	Capacitance of parallel plates in vacuum
ε_0	Permittivity of free space
ε^*	Complex permittivity
ε^*_r	Relative complex permittivity
ε_r'	Relative dielectric constant
ε_r''	Relative dielectric loss factor
$\tan\delta$	Dielectric loss tangent
I_{cal}	Calculated intensity
hkl	Miller Indexes
C_{hkl}	Correction due to experimental geometry set-up
F_{hkl}^2	Structure factor
I_{bck}	Refinement Parameter: Background
P_{hkl}	Refinement Parameter: Peak Profile
ω	Angular frequency
ω	Angular frequency
ω_{max}	Angular frequency at corresponding peak
X	Reactance
j	Imaginary part,$\sqrt{-1}$
Z^*	Complex Impedance
Z'	Real part of impedance
Z''	Imaginary part of impedance
M^*	Complex electric modulus
M'	Real part of electric modulus
M''	Imaginary part of electric modulus

M_{max}	the value of M" peak
f_M	Peak frequency
Y^*	Complex admittance
Y'	Real part of admittance
Y"	Imaginary part of admittance
χ_e	Dielectric susceptibility of the medium
χ_e	Dielectric susceptibility of the medium
l	Length
ρ	Resistivity
σ	Conductivity
σ_{dc}	DC conductivity
σ_{ac}	AC conductivity
s	Frequency exponent
E_g	Energy gap
K	Thermal conductivity
α	Thermal diffusivity
ρ	Density
c	Specific heat capacity
$\dot{Q}$	Heat transfer
T	Temperature, K
wt%	Weight percentage
mol%	Mol percentage
W_i	Weight fraction
S_i	Scale factor of phase i
Z	Number of formula units per unit cell
M	Mass of the formula unit
V	Volume of the unit cell
ΔE	Activation Energy
ΔE_{dc}	Activation Energy for DC conduction
ΔE_{ac}	Activation Energy for AC conduction
K_B	Boltzmann constant
σ_o	Pre-exponential factor
τ	Relaxation time
τ_o	Pre-exponential factor or the relaxation time at infinite temperature
τ_{gb}	Grain boundary relaxation time
τ_g	Grain relaxation time
ΔE_R	Activation energy of relaxation process
Y_o, n	Parameter of CPE
χ^2	Chi square

LIST OF ABBREVIATIONS

SS	Conventional solid state
MA	Mechanical alloying
MM	Mechanical milling
MnO_2	Manganese (IV) oxide
Mn_2O_3	Manganese (III) oxide
V_2O_5	Vanadium pentoxide
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscopy
PVA	Polyvinyl alcohol
ICSD	Inorganic Crystal Structure Database
AC	Alternating current
DC	Direct current
g	Grain
gb	Grain boundary
CPE	Constant phase element

CHAPTER 1

INTRODUCTION

1.1 Background of project and motivation

Currently, composite materials have wide variety of applications in our daily life such as electrical devices, mobile communication systems, etc. Therefore, composite tailoring was set off to suit the particular needs for different usages.

In the past decade, there have been several research carried out with different metal oxides due to their applications in various electronic devices such as smart window (Zhangli et al., 2013), optical detector (Bin et al., 2013), cathode coating in high-capacity lithium batteries (Di Blasi et al., 2015), high performance capacitor (Vilar et al., 2005), thermistor (Gouda et al., 2013) and others.

Transition element has mixed valence ions, hence those compounds have unique properties and very useful in various fields. Manganese is one of the transition element which has a formal oxidation state from -3 to +7. Meanwhile, manganese oxides include MnO, Mn_2O_3, Mn_2O_7, etc (Kemmitt et al., 1975). According to pervious researches, composites containing MnO_2 such as V_2O_5 (Gouda et al., 2009), SnO, As_2O_3 (Kayan et al., 2004), CaO (Vilar et al., 2005), Fe_2O_3 (Molenda et al., 1987) etc were investigated.

Besides, vanadium oxides which include V_2O_3, V_2O_5, V_6O_{13}, VO_2, etc., show a phase transition from the semiconductor phase to the metal phase when measuring temperature increases (Xiaochun et al., 2008). Therefore, the phase change gives more variations of electrical and dielectric properties.

From previous study, Gouda et al. (Gouda et al., 2009) prepared mixed oxides of Mn and V under different mass ratio of Mn_2O_3 and VO_2 from 90:10 to 5:95. They found that resistivity and thermistor constant of beta or gamma form of $Mn_2V_2O_7$ are higher compared to the well known oxides of vanadium and binary/ternary oxides of manganese, nickel and cobalt. It meant that d-block electronic configuration of V^{5+} in $Mn_2V_2O_7$ contributed to higher resistivity (Bordeneuve et al., 2009).

There were some works related with V_2O_5 done previously, but the reports were focused on structural investigation and some electrical properties of MnV_2O_6 and $Mn_2V_2O_7$ (Gouda et al., 2013; Gouda et al., 2009; Dongfang, 2013; Mocala et al., 1987). However, it still lacks a comprehensive electrical studies on Mn-V oxide system which can gives insight into the response of grain and grain boundary to the electric field. Also, there were several investigations related to Mn and V oxides reported prepared by different methods which were pulsed laser deposition (Dongfang, 2013), solid state reaction (Gouda et al., 2009, Mocala et al., 1987) and high pressure synthesis (Subramanian,

1992). However, there are no studies on Mn-V oxide prepared by mechanical alloying method. Therefore, it is a pioneer work in this project. According to previous studies, the Mn-V mixed oxides prepared in this project may have high dielectric loss factor and the energy loss may convert into heat. Hence, thermal diffusivity measurement was carried out to further understand the thermal properties of the mixed oxides.

In this project, the conventional solid state and mechanical alloying method were employed to prepare the samples. The aim is confined to study the morphology and the phase composition of Mn-V oxides produced at different sintering temperatures. Also, the electrical and dielectric properties of the mixed oxides at different measuring temperature were also investigated. Lastly, the thermal diffusivity of the mixed oxides was measured at different temperatures as subordinate studies in this project.

1.2 Transition Metal

In the periodic table, the transition metals are any element in d-block of the periodic table. These elements have partially filled d sub-shell which can give up their valence electrons to become cation. Therefore, the d-orbitals have variety of oxidation states.

The general properties of the transition metals are usually high melting point, have several oxidation states, form coloured compounds and paramagnetic (HyperPhysics, n.d.). Transition metal oxides are starting to draw attention from many researchers, because they have wide range of electronic properties ranging from insulating, semiconductor and conducting properties. Their electronic properties can be modified by changing its morphology structure, doping or changing their stoichiometry. The plentiful of transition metal oxides in nature is another advantage for technologies to be widely utilized (Walia et al., 2013).

1.2.1 Manganese Oxide

Manganese element is one of a transition metal which is hard and bronze in color. It is one of the transition elements which have a wide range of oxidation states such as +2, +3, +4, +6, and +7. The electron configuration of manganese element is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$. The melting point of manganese metal is relatively high which is 1244 ^oC (Kemmitt et al., 1975). It occurs naturally as the mineral pyrolusite, which is an essential ore of manganese (Anthony et al., 1990). On the other hand, manganese oxides basically include MnO, Mn_3O_4, Mn_2O_3, MnO_2 with different allotropes which show some advantages of non-toxicity, easy to obtain and therefore low cost. Moreover, they exhibit high specific capacitances and have become the most promising materials in application of supercapacitors (Junhua et al., 2002).

Manganese (IV) oxide is the one of the starting materials in this project. It is also known as manganese dioxide, MnO_2 with +4 oxidation state. MnO_2 has blackish or brown solid physical appearance. MnO_2 melts at 535^oC (MSDS, n.d.) and insoluble in water. The

basic unit of MnO_2 is octahedral closed packet structure, which is built up by one manganese atom coordinated with six oxygen atoms (Figure 1.1). The atoms are linked together in different ways so as to form various crystallographic and derivative structures (Inorganic Crystal Structure Database, 2014).

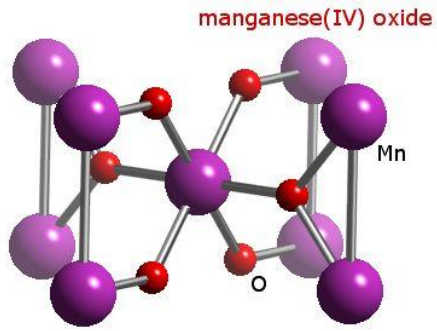

Figure 1.1: Tetragonal crystal system of MnO_2.
(http://www.webelements.com/compounds/manganese/manganese_dioxide.html)

Naturally, MnO_2 with different structural forms has been found, which are α-, β-, δ-, γ- and ε-MnO_2 which have various properties (Zhong Jie et al., 2015; Hongtao et al., 2012). The α-MnO_2 phase has nanowire structure where β-MnO_2 phase has mircorods structure (Bang et al., 2014). The different morphologies structures of manganese oxide can result in the change of crystal lattice, the differences of crystal defects and holes, which affect the polarization and consequently alter the dielectric properties of materials. According to the morphological structure, mircorods have less polarization ability than nanowires, hence α-MnO_2 has higher dielectric permittivity compared β-MnO_2. Also, the temperature will affect the movement of charge carriers in the interior tunnels and cavities which leads to the fact that MnO_2 materials will have various dielectric relaxation phenomena and electromagnetic characteristics (Yude et al., 2010; Hongtao et al., 2010).

Nowadays, MnO_2 is widely studied because of its interesting fundamental physical properties. They have lots of applications such as, catalyst, molecular-sieves, ion-sieves due to it ion exchange, molecular adsorption, electrochemical and magnetic properties (Yude et al., 2010). It is also used in preparing soft magnetic materials, electrodes and electrochemical capacitors (Dakhel, 2006).

1.2.2 Vanadium Oxide

Vanadium element has an atomic number of 23 and the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. Vanadium element is a transition metal element which has variation of oxidation states ranging from +5, +4, +3 to +2. Therefore, it exists in many phases such as VO, VO_2, V_2O_3 or V_2O_5 (Walia, et al. 2013). V_2O_5 is a brown or yellow solid. It is an amphoteric oxide and oxidizing agent (Zabriky, 2009).

The other phases of vanadium oxide (VO, VO_2, V_2O_3) have multiple crystal phases, but V_2O_5 exists only as an orthorhombic crystal (Figure 1.3) which is fundamentally comprising of VO_5 pyramids that form alternating double chains along the b-axis (Walia et al., 2013). Hence, V_2O_5 has a strong tendency for the crystallites in a powder or a texture to be oriented or grew in belt shapes (Sharma et al., 2015).

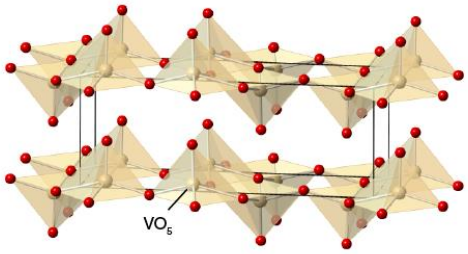

Figure 1.2: Orthorhombic crystal system of V_2O_5.
(http://www.chemtube3d.com/solidstate/SS-V2O5.htm)

Among the oxides of vanadium, V_2O_5 melted at 690°C (MSDS, n.d.), an orange-red powder and partially soluble in water to give a pale yellow acidic solution, and which dissolves readily in alkalies to form vanadates. Meanwhile, it is also soluble in strong acids. V_2O_5 is widely used in analytical chemistry due to the V_2O_5 ion can form slightly soluble or intensely colored, simple or complex compounds with inorganic and organic substances (Manskaya et al., 1968).

V_2O_5 is widely used in thin-films device application due to its phase transition behavior. When the vanadium oxide thin film was heated to a specific temperature, it will present a phase transition indicated by the changes of its electrical and optical properties (Ya et al., 2014). An insulating thin film with good dielectric properties also has wide range of applications in various electronic devices, hence the dielectric properties of V_2O_5 thin film has drawn much attention from researchers (Thomas et al., 1989).

1.3 Conventional Solid State Method

Conventional solid state method is widely used to prepare polycrystalline solid from mixture of starting materials. Furthermore, this method is low cost and high yield which is another advantage to become a preference of many researchers. In recent years, the materials synthesis and processing become crucial for materials development. As a result, the importance of sintering increases as materials processing technology.

The purpose of the sintering process is to produce sintered parts with reproducible and designed microstructure through controlling the sintering variables. Microstructure control means the control of grain size, sintered density, size and distribution of other

phases including pores. Sintering processes can be categorized into two types: solid state sintering and liquid phase sintering. Solid state sintering occurred when the powder pelletized or densified completely in a solid state at the sintering temperature. At higher sintering temperatures, liquid phase sintering occurs in the powder compact during sintering.

The sinterability and sintered microstructure of a powder compact were determined by several variables. They may divide into two categories: materials variables and process variables. The materials variables include chemical composition of powder compact, size, shape, size distribution, etc. These variables influence densification and grain growth. The homogeneity of the powder mixture also takes a significant role. The other variables related to sintering condition (process variables) are mostly thermodynamic variables, such as temperature, time, pressure, atmosphere, heating and cooling rate, etc (Randall, 1996).

1.4 Mechanical Alloying Method

Mechanical alloying is a dry, solid state powder, high-energy ball milling technique. This technique has been widely used to produce a variety of commercially usages and scientific purposes.

Usually we can easily found two terms used in the literature to denote the processing of powder particles in high-energy ball mills. Mechanical Alloying (MA) describes the process when mixtures of powders (metals or alloy) are milled together. However, the milling of uniform composition powders, such as pure metals, intermetallics, or prealloyed powders for a reduction in particle size, but not for the materials homogeneities, has been named as Mechanical Milling (MM) (Suryanarayana, 2001).

MA is a well-known high-energy ball milling method for materials in powder form which requires neither high temperature or heating nor using expensive equipment (Loginov et al., 2015). The powders are trapped between the grinding balls in a vial during milling. The powder particles undergo repeated severe plastic deformation and fracture processes, resulting incorporation of lattice defects and to a continuous refinement to the nanocrystalline size. On the other hand, the milling conditions also played important roles in the milling process. For instance, the mechanical behavior of the powder components such as, their phase equilibria, and the stress state during milling can then result in intermixing, solid state interdiffusion and supersaturation beyond the equilibrium solubility limit and chemical reaction, lastly resulting in metastable phase formation (Suryanarayana, 2001; Eckert et al., 1991; Raanaei et al., 2015; Scudino et al., 2009).

This method carried out by using SPEX SamplePrep 8000D Mixer/Mill (Figure 4.1), are able to mill about 8-20 g of the powder at a time depending on the size of the vials (Figure 4.2). The grinding balls move energetically back and forth for several thousand times a minute, thus crushing and milling the powders and consequently, a homogeneous mixed

composites with smaller particle size powders was obtained (Loginov et al., 2015; Azimi et al., 2014).

1.5 Objective

1. To prepare and characterize mixed oxides 60 mol% of $2MnO_2$ and 40 mol% V_2O_5 by conventional solid state reaction method and mechanical alloying method at different sintering temperatures, 500°C - 800°C.
2. To study the morphology and phase composition changes of the samples at different sintering temperatures.
3. To study the electrical and thermal properties of different Mn-V oxides phases under different measuring temperatures, 30°C - 400°C.

1.6 Hypothesis

1. The average grain size would increases with sintering temperature.
2. Phase composition of starting materials would decrease while phase composition of Mn-V oxides would increase with sintering temperature.
3. Electrical conductivity, dielectric constant and dielectric loss factor of the samples would increase as measuring temperature increases. And**,** thermal diffusivity would decreases with increase in measuring temperature.

1.7 Outlines of the Present Study

The present thesis consists of 6 chapters. First of all, Chapter 1 briefly presents the background and the importance of the project followed by the introduction of the preparation techniques used in this project which are conventional solid state method and mechanical alloying method. The introduction of the starting materials manganese oxide and vanadium oxide are also included, followed by the objectives of this research. Chapter 2 deals with the previous published works which are related to the present study. Chapter 3 discussed the mechanism regarding sample preparation methods, theory and basic principles related to this study. Chapter 4 mainly describes the experimental methodology for the preparation of the mixed oxide of Mn and V which are conventional solid state and mechanical alloying methods. From the flow charts, the procedures of sample preparation are completely presented with detail description of each procedure using two methods followed by the details of dielectric measurement and characterization techniques. Chapter 5 presents the discussion toward the results obtained, comparison between the samples at different sintering temperatures, measuring temperatures and frequencies. Lastly, Chapter 6 summarizes all the results and presented significant results and conclusion. Some recommendations for future work related to this research are also suggested.

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