NiO MODIFICATION USING Zr^{4+} AND Ca^{2+} FOR DIELECTRIC IMPROVEMENT

by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles "Dielectric Properties Modification of NiO Using Zr^{4+} and Ca^{2+}". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABREVIATION

$Ni_{(1-x)}Zr_xO$	ZrO_2 doped NiO with *x* mole fraction of Zr
$Ni_{(1-x)}Ca_xO$	CaO doped NiO with *x* mole fraction of Ca
FESEM	Field Emission Scanning Electron Microscopy
XRD	X-ray Diffraction

LIST OF SYMBOLS

%	Percentage
<	Less than
>	More than
°	Degree
°C	Degree Celsius
°C/min	Degree Celsius per minute
MPa	Mega Pascal
mg	Miligram
g	Gram
h	Hour
s	Second
min	Minutes
µm	Micrometer
mm	Millimetre
cm	Centimeter
m	Meter
wt %	Weight percent
A	Amper

V	Voltage
s	Second
d	Thickness
tan δ	Tangent loss or dissipation factor
ε	Permttivity
λ	Wave length
T	Temperature
g/cm^3	Gram per cubic centimeter
MHz	Megahertz
GHz	Gigahertz
kHz	Kilohertz

MODIFIKASI NiO MENGGUNAKAN Zr^{4+} DAN Ca^{2+} UNTUK PENAMBAHBAIKAN SIFAT DIELEKTRIK

ABSTRAK

Dalam kajian ini, kesan bahan dop ion zirconium (Zr^{4+}) dan ion kalsium (Ca^{2+}) ke atas sifat-sifat dielektrik NiO dikaji. Bahan elektroseramik $Ni_{(1-x)}Zr_xO$, $Ni_{(1-x)}Ca_xO$ dan $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ telah dihasilkan melalui kaedah tindak balas keadaan pepejal. Tiga bahan mentah utama iaitu NiO, ZrO_2 dan CaO melalui pencampuran basah selama 24 jam, kemudian dikalsin pada suhu 1000ºC. $Ni_{(1-x)}Zr_xO$ dan $Ni_{(1-x)}Ca_xO$ masing-masing disinter pada suhu 1280°C selama 10 jam dan 1250°C selama 4 jam. Manakala $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ disinter pada suhu 1200ºC, 1250ºC and 1300ºC selama 5 jam. Suhu 1250ºC selama 5 jam telah dikenalpasti sebagai parameter pensinteran yang optimum dalam pembentukan $Ni_{0.95}Zr_{0.02}Ca_{0.01}$. Ujian XRD ke atas sampel yang disinter menunjukkan pembentukan fasa $Ni_{(1-x)}Ca_xO$, $Ni_{(1-x)}Zr_xO$ dan $Ni_{0.95}Zr_{0.02}Ca_{0.01}$. Pemerhatian FESEM ke atas sampel $Ni_{(1-x)}Zr_xO$ menunjukkan saiz butiran semakin besar dengan penambahan bahan dop dan $Ni_{(1-x)}Ca_xO$ menunjukkan saiz butiran semakin besar dengan penambahan bahan dop. Manakala saiz butiran $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ semakin membesar dengan peningkatan suhu pensinteran. Ketumpatan $Ni_{(1-x)}Zr_xO$, $Ni_{(1-x)}Ca_xO$ dan $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ semakin meningkat dengan penambahan bahan dop Zr^{4+} dan Ca^{2+}, dan keliangan semakin menurun dengan peningkatan kepekatan bahan dop. Pemalar dielektrik $Ni_{(1-x)}Zr_xO$ dengan x = 0.02 mol % Zr^{4+} menunjukkan pemalar dielektrik tertinggi (700) dan nilai lesapan dielektrik adalah sederhana (0.16). Manakala sifat

dielektrik bagi sampel $Ni_{(1-x)}Ca_xO$ yang didop dengan x = 0.01 mol % Ca^{2+} mempunyai lesapan dielektrik terendah (0.05) tetapi sederhana dalam pemalar dielektrik (123), diukur pada frekuensi 1 MHz. Kombinasi dua bahan dop yang optimum ini, iaitu Zr^{4+} = 0.02 mol % dan Ca^{2+} = 0.01 mol %, telah digunakan untuk menghasilkan $Ni_{0.95}Zr_{0.02}Ca_{0.01}$. Sifat dielektrik bagi $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ mempunyai pemalar dielektrik tertinggi (727) dan nilai lesapan dielektrik terendah (0.04).

NiO MODIFICATION USING Zr^{4+} AND Ca^{2+} FOR DIELECTRIC IMPROVEMENT

ABSTRACT

In this research, the effect of Zirconium ions (Zr^{4+}) and Calcium ions (Ca^{2+}) dopant on NiO was investigated. The electroceramic of $Ni_{(1-x)}Zr_xO$, $Ni_{(1-x)}Ca_xO$ and $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ was prepared by using solid state reaction method. Three main raw materials of NiO, ZrO_2 and CaO were mixed for 24 hours, then were calcined at 1000ºC. $Ni_{(1-x)}Zr_xO$ and $Ni_{(1-x)}Ca_xO$ was sintered at 1280°C for 10 hours and 1250°C for 4 hours, respectively. $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ was sintered at 1200ºC, 1250ºC and 1300ºC for 5 hours. The 1250ºC for 5 hours was identified as optimum sintering profile for $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ formation. XRD analysis on sintered sample showed the single phase formation of $Ni_{(1-x)}Zr_xO$, $Ni_{(1-x)}Ca_xO$ and $Ni_{0.95}Zr_{0.02}Ca_{0.01}$. FESEM observation on the $Ni_{(1-x)}Zr_xO$ showed that grain size are bigger with increasing amount of dopant and $Ni_{(1-x)}Ca_xO$ shows that grain size are getting larger with increasing amount of dopant. Meanwhile the grain size of $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ are larger with the increasing sintering temperature. The densification of $Ni_{(1-x)}Zr_xO$, $Ni_{(1-x)}Ca_xO$ and $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ was improved using Zr^{4+} and Ca^{2+} doping and the porosity decrease at higher dopant concentration. The dielectric behavior of $Ni_{(1-x)}Zr_xO$ with x = 0.02 mole % Zr^{4+} exhibited highest dielectric constant (700) with moderate dielectric loss (0.16). Meanwhile, the dielectric behavior of $Ni_{(1-x)}Ca_xO$ samples show that the sample doped with x = 0.01 mole % Ca^{2+} obtained the lowest dielectric loss (0.05) but moderate in dielectric constant (123), measured at 1 MHz. The combination of this two optimum dopant content, Zr^{4+} = 0.02 mole % and

Ca^{2+} = 0.01 mole %, has been applied to produce $Ni_{0.95}Zr_{0.02}Ca_{0.01}$. The dielectric behavior of $Ni_{0.95}Zr_{0.02}Ca_{0.01}$ posses the highest dielectric constant (727) and lowest dielectric loss (0.04).

CHAPTER 1

INTRODUCTION

1.1 Ceramic Materials

Ceramics is an inorganic compound consisting of metallic and nonmetallic elements such as silicon nitride (Si_3N_4), alumina (Al_2O_3) and silicon carbide (SiC). It is mainly categorized as oxide, nitride, carbides and borides prepared by the action of heat and subsequent cooling (Setter and Waser, 2000). Ceramic materials generally withstand high temperatures that range from 1000°C to 1600°C, are brittle with low toughness, ductility, strong in compression and weak in shearing/tearing (Lehman et al., 1999).

Ceramics are usually good thermal and electrical insulators due to the stability of their strong bond. The properties of these ceramics are also comparable and sometimes better than existent materials since the cost of ceramic materials is cheaper compared to other materials. Moreover, ceramic materials have been traditionally admired for their unique electrical, optical and magnetic properties which become more important technologies including communication, energy conversion, storage, electronics and automation (Moulson and Herbert, 2003).

Ceramic can be divided into two parts which are traditional ceramics and advanced ceramics. Traditional ceramic can be characterized by mostly silicate-based porous microstructures that are coarse, nonuniform and multiphase. Some examples of traditional ceramics are porcelain, glass, bricks and refractory materials. Advanced

ceramic refers to engineering ceramics featuring electrical, electronic and magnetic properties. Advanced ceramic is categorized as electroceramics, bioceramic, glass ceramics, and others. Electroceramics are used to explain ceramic materials formulated for electrical, magnetic or optical properties.

Nowadays the communication technology developments are moving to wireless technology such as cellular phones and global positioning systems. These developments of ceramic materials have produced a lot of material depending on the processing method, structure and physical device (Askeland and phule, 2003). There have been reports that ceramic was first used in the electronic industry as electrical conductors. These properties can be modified or designed in order to produce device with higher dielectric constant (Naidu, 2009). Examples of electrical properties are resistivity, conductivity, dielectric constant, dielectric loss, dielectric strength and capacitance. Due to this demand, much research has been done on ceramic materials to produce a material with high dielectric constant and low dielectric loss (Agrawal, 1998).

Electroceramic materials that have high dielectric constant can be used for construction of ceramic capacitor. Capacitor is an important element in electrical and electronic circuit. In this case, higher dielectric material in the range of 100 kHz to 1 GHz is required to maintain or increase the capacitance when the miniaturizing process is applied to devices (Askeland and phule, 2006). Dielectric materials with high electrical resistance can support the electric field efficiently. Lowering dielectric loss will increase the efficiency of dielectric material. The term dielectric material is used to

explain the electrical insulator that can be sustained with a minimal dissipation of power (Kao, 2004).

The ideal dielectric material does not exhibit electrical conductivity when an electric field is applied. In practice all dielectrics do have some conductivity, which generally increases with the increase rise of temperature and applied field. If the applied field increases to some critical magnitude, the material abruptly becomes conductive. A large current flow and local destruction occurs to an extent depending upon the amount of energy which the source supplies to the low conductivity path (Mcgraw, 2005). One of the materials that can be used as high dielectric constant material is NiO. NiO is known as one of the electroceramic materials and is a very interesting material due to its anti-fferomagnetic structure which is, the magnetic moments of atoms or molecules, usually related to the spins of electrons, aligned in a regular pattern with neighboring spins (on different sublattices) pointing in opposite directions. Stoichiometric NiO ($Ni_{50}O_{50}$) is a Mott-Hubbard insulator with room temperature conductivity of less than 10^{-13} S cm^{-1}. Very low conductivity of NiO may be due to hopping of charge carriers associated with Ni^{2+} vacancies (Gokul et al., 2013).

NiO also has good temperature stability in a wide temperature range of 100–150ºC. NiO is different from other materials that have ferroelectric properties. Near Curie point, $BaTiO_3$ shows a great enhancement in dielectric constant but it also has unfavorable structural phase transitions due to strong temperature dependence. Meanwhile, the permittivity of NiO is stable above -73ºC. The dielectric constant of NiO

was found to drop rapidly to a value around 100 when the temperature was below -173 ^{o}C but was not accompanied by any structural phase transition (Maensiri et al., 2007).

1.2 Problem Statement

Nowadays, commercial micro-electroceramics technologies, such as capacitor and memory devices, place increasing demands on the performance of high dielectric permittivity and low dielectric loss in the frequency range (medium wave) broadcast, amateur radio and avalanche beacons. In the early electronic and electrical systems, large dielectric constant was observed in perovskite and ferroelectric oxides (Tangwancharoen et al., 2009).

Perovskite structures such as $PbZrTiO_3$ (PZT) and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), exhibit high dielectric constant but both materials have high dielectric loss and also poor temperature stability (Bencan et al., 2012). Besides, they contain lead which is toxic. Most recently, a lead-free perovskite like $CaCu_3Ti_4O_{12}$ (CCTO) has high static dielectric constant at room temperature but its weak temperature is between -173 and 107 ^{o}C (Guillemet et al.,2006). The key properties required for a capacitor are high dielectric permittivity and low dielectric loss which can withstand high temperatures. A few researchers observed that the giant dielectric constant is related to the microstructure of the material. Dispersion of metallic Ni particles into ceramic $BaTiO_3$ produces a high dielectric constant (8×10^4) (Manna et al., 2008). The giant dielectric constant is found in electron doped manganites, $LaMnO_3$. CCTO exhibits an unusually high dielectric constant of (10^4–10^5) at room temperature (Wu et al., 2002). Large dielectric constants of $LaMnO_3$ and CCTO are interpreted by polarization mechanism from electrically

heterogeneous grain and grain boundary regions (Li et al., 2012), but the dielectric loss of the system is high. However, it is difficult to achieve these two properties simultaneously in a particular material (Wu et al., 2003).

However, there are several weaknesses of NiO. For undoped NiO, the dielectric constant (ε_r) = 30 at 100 KHz is lower compared to doped NiO. According to Jana et al., 2007, Potasium, Titanium doped Nickel Oxide (KTNO) shows larger decreasing value of ε_r at higher frequency. The introduction of Ni^{2+} vacancies caused a considerable increase in dielectric properties of NiO, however it contains a large number of vacancies and the grain boundary of all KTNO samples causes high probability of inter well hopping (long range hopping) and it affects dielectric relaxation at high frequency. In the NiO materials, there are plenty of defects and control over those defects is a challenging process. These defects have significant influence on the properties of NiO. Hence, controlling the defects such as structural and compositional defects, will lead to tailoring the properties of ceramics (Atkinson et al., 1980). Although properties of NiO have been studied before, not much work has been reported on the dielectric properties of NiO at high frequency. Dielectric constant and loss properties were studied by Mallick and Mishra. (2012), and revealed that Ni^{2+} or oxygen vacancies affected the electrical properties of NiO.

In order to achieve these two important properties, high dielectric constant and low dielectric loss in capacitor and memory devices, many materials have been studied and NiO has been found to be one of the promising materials to be used as various applications in supercapacitor, exchange bias controlled spin valve and electrochromic

devices and independent with a high temperature (Cletus, 1993). Pure NiO is an insulator at room temperature, nonperovskite, lead free and nonferroelectric (Dutta et al., 2010).

The improvement in dielectric properties of NiO becomes very important due to its complex band structure in which the dielectric properties can be tailored by introducing other element into the system. Chen et al. (2004) and Dakhel, (2012) studied the dielectric properties of NiO at low frequency. Both reports revealed that dielectric constant for pure NiO was 30 and oxygen vacancies were responsible for the dielectric properties of Ni. Several dopants of varying valencies, ionic size and concentrations were added into NiO and the variations in densification, and dielectric properties of NiO were reported. Thus, much research has been carried out to improve dielectric properties by applying dopants into NiO.

Meanwhile, the increase in value for small amounts of doping is attributed to the increase in the density and grain growth. However, when the amount of dopant added is too high (>2mol %), the density of NiO will decrease. It was found that Ca has been used in $Ba_{1-x}Ca_xTiO_3$ system and it was reported that the dielectric loss was suppressed when the Ca dopant was increased (Chen et al., 2004). The dielectric properties increased when the ionic radii of the dopant was close to NiO's ionic radii which was 0.069 nm (Siddiqui et al., 2012).

Several researchers also studied the effect of ZrO_2 on dielectric properties of NiO. They claimed that with the addition of ZrO_2 as a dopant, the dielectric properties of NiO, especially dielectric constant, could be improved. Chen et al. (2009) concluded that

NiO with $x = 0.1$ had dielectric constant of around 10^4 at 1 kHz. It was better compared with the undoped NiO sample that could only exhibit 30 at 1 kHz.

Recent works were focused on the effect of various dopants on the properties of NiO. However, there are no studies on the properties of $Ni_{0.95}Zr_{0.02}Ca_{0.01}O$ at higher frequencies 1 MHz to 1 GHz. Nowadays, there are many devices that operate at high frequency such as wireless communication devices. As NiO has potential for high frequency devices application, the knowledge of high frequency properties of NiO is also necessary. Thus, this work focuses on the effect on the structural and electrical properties of $Ni_{(1-x)}Zr_xO$, $Ni_{(1-y)}Ca_yO$, and $Ni_{(1-x-y)}Zr_xCa_yO$. Zr^{4+} and Ca^{2+} with atomic radii of 0.079 nm and 0.100 nm, and have the potential to be doped into NiO because they tend to disturb the NiO structure, hence improve the dielectric properties of NiO at room temperature at high frequency range from 1MHz to 1GHz. In this study, in order to achieve high dielectric constant and low dielectric loss, Zr^{4+} and Ca^{2+} were doped into the NiO system.

1.3 Research Objectives

This study focuses on dielectric properties of undoped and doped NiO and characterization of various doping elements by the solid state method. Therefore, the main objectives are:

1) To synthesis Zr^{4+} and Ca^{2+} doped NiO through solid state reaction.

2) To investigate the crystal structure and morphology of Zr^{4+} and Ca^{2+} doped on NiO samples.

3) To investigate the effect of NiO doped with Zr^{4+} and Ca^{2+} dopant on the dielectric properties (ε_r and tan δ) of NiO measured at 100 Hz -1 GHz.

1.4 Scope of Study

NiO compound has recently attracted considerable research interest due to high dielectric constant and low dielectric loss. In order to improve its dielectric properties, the current study focused on the process, properties, structure relationship of the high dielectric properties of NiO by doping with different mole% of Zr^{4+} and Ca^{2+}. Doping methods open an effective way to alter the dielectric performance which is essential for microwave communication application. Five different mole% of dopants were selected with variation of doping concentration. They were 0.01, 0.02, 0.03, 0.05 and 0.10 mole% of Zr^{4+} and Ca^{2+}. The aim of this work is to investigate the effect of different dopant concentration on the properties of NiO with various Zr^{4+} and Ca^{2+} compositions at higher frequencies (1 MHz to 1 GHz). So, a further study of NiO with different mole% of Zr^{4+} and Ca^{2+} will be investigated in this project.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Electroceramic is a class of ceramic material used primarily for their electrical, mechanical, thermal and chemical stability. These unique properties have become increasingly important in many key technologies including energy conversion, electronic and automation. The various subclasses of electroceramic have parallel growth of new technologies including ferroelectric, ferrite, solid electrolytes, piezoelectric and semiconducting oxides (Moulsons and Herbert, 1992). Electroceramic used for microwave device application need good dielectric properties which are high ε_r >1 and low tan δ <0.001 (Belous and Ovchar, 2010). High ε_r has been found in perovskite ferroelectric oxide (Manna et al., 2008).

A ceramic capacitor is a fixed value capacitor in which ceramic material acts as the dielectric constant and loss. It is constructed of two or more alternating layers of ceramic and a metal layer acting as the electrodes. The composition of the ceramic material defines the electrical behavior and therefore applications. Ceramic capacitors can be divided into two which are ceramic capacitors offering high stability and low losses for resonant circuit and ceramic capacitors offering high volumetric efficiency for buffer, by-pass and coupling applications.

Examples of electroceramics application are zinc oxide for varistors, lead zirconium titanate (PZT) for piezoelectrics, barium titanate in capacitors, tin oxide as

gas sensors (Hammani et al., 2008). Lead lanthanum zirconium titanate (PLZT) and lithium niobate for electro-optic devices (Graettinger et al., 1991). Lunkenheimer et al. (2004) found that CCTO exhibited unusual ε_r of 10^4-10^5 at room temperature. The high ε_r arose due to structural distortion at ferroelectric transition in ferroelectric and relaxor materials (Manna et al., 2008). The grain boundaries, bulk material and surface effect are the main points for better results in dielectric constant and dielectric loss (Dutta and De, 2007). The different classes of electroceramic materials have their own dielectric constant and dielectric loss due to different properties of the material.

2.2 Microwave Communications

Electromagnetic waves travel in a straight line at approximately the speed of light and are made up of magnetic and electric fields that are at right angles to each other and to the direction of propagation (Tomasi, 2004). Modern microwave and radio frequency (RF) engineering was widely used due to the explosion in demand for voice, data and video communication capacity (Golio et al., 2001). Microwave technology almost controlled the communication industry because was an increase in demand for communications systems such as mobile telephones, broadcast video and GPS to environmental monitoring via satellites. Most of the microwave based device systems are located from the range 300 MHz to 300 GHz as shown in Figure 2.1 (Golio et al., 2001). The microwave region can be divided into three sections, ultra high frequency (UHF) region from 300 MHz to 3 GHz, super high frequency (SHF) region from 3 GHz to 30 GHz and extremely high frequency (EHF) region from 30 GHz to 300 GHz (The Spectrum Plan, 2006). Compared to radio waves, microwave can carry more information

because of its higher frequency and shorter wavelength (λ). Higher frequency can produce large BW that can achieve higher data transmission rates while the short λ allows the energy to be concentrated into a small area.

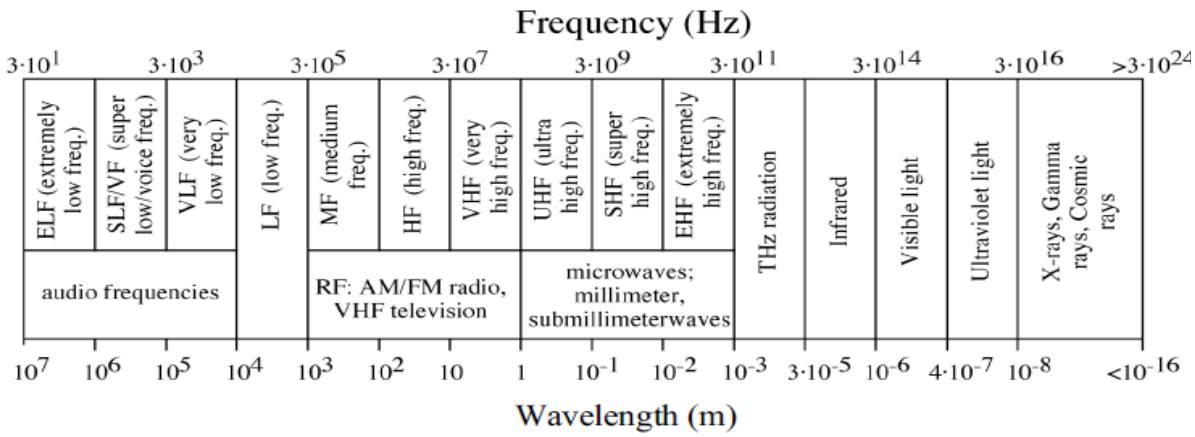

Figure 2.1: Microwave spectrum and applications (Golio et al., 2001).

2.3 Dielectric Materials

Dielectric materials are ceramic materials that are good electrical insulators. Although these materials do not conduct electric current when electric field is applied, they are not inert to the electric field (Moulson and Herbert, 2003). The field causes a slight shift in the balance of charges within the material to form an electric dipole, thus it is called "dielectric". When dielectric material is placed in an electric field, electric charges do not flow through the material as in a conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. These materials have positive charges that are displaced along the field and negative charges that shift in the opposite direction (Callister and Rethwisch, 2012).

Although the dielectric materials are poor conductors of electricity, they are efficient supporters of electrostatic fields. An electrostatic field can store energy if the flow of current between opposite electrically charged poles is kept to a minimum while the electrostatic lines of flux are not impeded or interrupted (Huang, 2009). Another importance of the materials is the ability to support an electrostatic field while dissipating minimal energy in the form of heat (Moulson and Herbert, 1990).

The lower the dielectric loss (the proportion of energy lost as heat), the more effective is a dielectric material. Another consideration is the dielectric constant, the extent to which a substance concentrates the electrostatic lines of flux. Substances with a low dielectric constant include a perfect vacuum, dry air, and most pure, dry gases such as helium and nitrogen. Materials with moderate dielectric constants include ceramics, distilled water, paper, mica, polyethylene, and glass. Metal oxides, in general, have high dielectric constants.

The lower the dielectric loss which is the proportion of energy lost as heat, the more effective the dielectric properties of the material (Thostenson and Chou, 1999). Another consideration is the ε_r, the extent to which a substance concentrates as electrostatics lines of flux. Dielectric fulfill circuit functions as how their ε_r is directly proportional to the capacitance and also tan δ (Cava, 2001). This parameter is of primary importance which will affect the properties of the dielectric materials as stated before. Properties that will be discussed in the next chapter demand careful consideration in certain application of dielectric which are capacitance and tan δ (Jaffe et al., 1958).

2.4 Dielectric Properties

The main property of dielectric is being able to support the electrostatic field while dissipating minimal energy in the form of heat. The most common dielectric properties are ε_r and tan δ.

2.4.1 Dielectric Constant, ε_r

The ε_r is the ratio of the permittivity of a substance to the permittivity of free space. It is an expression of the extent to which material concentrates electric flux and is the electrical equivalent of relative magnetic permeability (Hench et al., 1990). As the electric flux density increases, the ε_r increase and all other factor remain unchanged. This enables objects of a given size, such as sets of metal plates, to hold their electrical charge for long periods of time, and to hold large quantities of charge. Materials with high ε_r are useful in the manufacturing of high-value capacitors (Brady and Clauser, 1991).

The capacitance is an important characteristic of dielectric materials. The capacitance of material is the relationship between the charge that was put on the material and its potential energy. Capacitance is the ability of a circuit system to store charges and a capacitor is a device in an electric circuit for storing electrical charges. If the charges on the plates are +Q and –Q, and V gives the voltage between the plates, the capacitance is given by Equation (2.1).

$$C = \frac{Q}{V} \qquad (2.1)$$

V is the voltage applied across the capacitor. The unit of for capacitance is Coulombs per volts, or Farads (F). When considering a parallel capacitor with a vacuum in the region between the plates as shown in (Figure 2.2 a), the capacitance can be computed from Equation (2.2).

$$C = \varepsilon_0 \frac{A}{l} \qquad (2.2)$$

A represents the area of the plates and *l* is the distance between them. The parameter ε_0, called the permittivity of a vacuum, is a universal constant having the value of 8.85×10^{-12} F/m (Brady and Clauser, 1991). If the dielectric material is inserted into the region within the plates as shown in (Figure 2.2 b), the capacitance can be computed from Equation (2.3).

$$C = \varepsilon \frac{A}{l} \qquad (2.3)$$

where ε, is the permittivity of this dielectric medium, which will be greater in magnitude than ε_0. Then, the dielectric constant or the εr can be obtained from Equation (2.4) by using this ratio

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \qquad (2.4)$$

The value is greater than unity and represents the increase in charge storing capacity by the insertion of the dielectric medium between plates. The ε_r is one of the material properties, which must be considered for capacitor design (Callister, 2007).

Referring to Figure 2.2, the relative permittivity ε_r increased after the dielectric material is inserted. The examples of ε_r values of some dielectric materials are listed in Table 2.1 (Kahn et al., 1988).

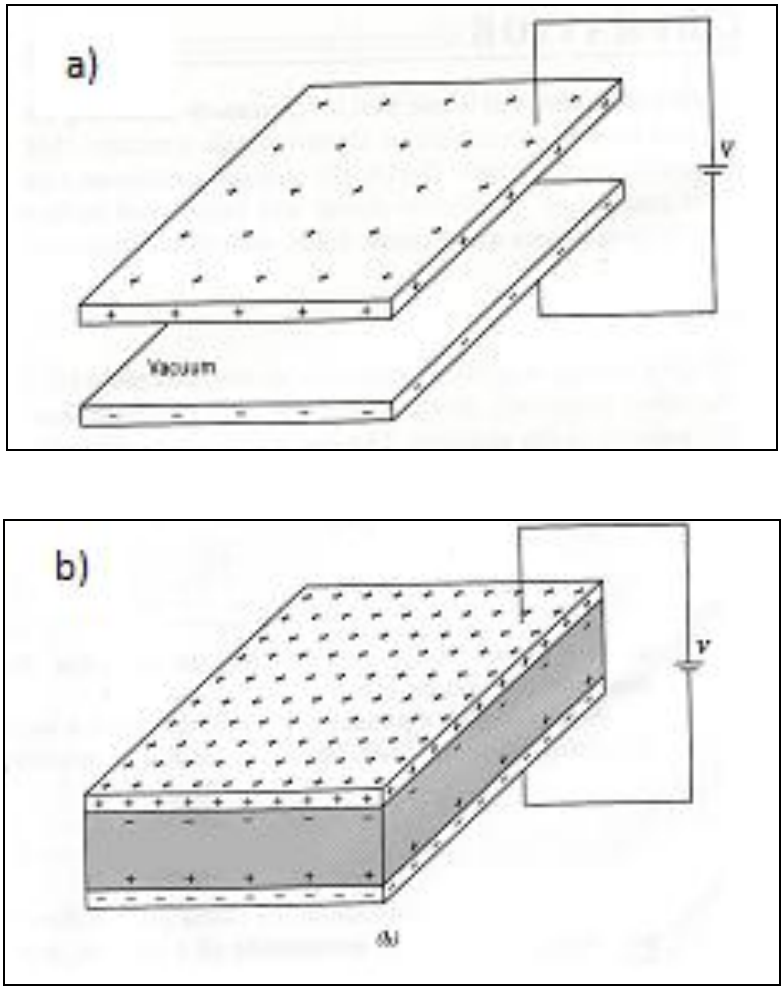

Figure 2.2: Parallel-plate capacitor (a) when a vacuum is present, and (b) when a dielectric material is present (Callister, 2007).

Table 2.1: Dielectric Constant at 25°C (Kahn et al., 1988).

Material	Dielectric Constant (ε_r)	Dielectric Loss (tan δ)
Air	1.00	-
Porcelain	5.5	3.75
Glass	7.75	1
Mica	5.40	1
Alumina	8.5	4
Rutile	80	0.375
Lead zirconate	110	30
Magnesium titanate	14	0.25
Strontium titanate	200	5
Calcium titanate	150	3

2.4.2 Loss tangent, tan δ

In the ceramic dielectric, losses will occur and specified by the dissipation factor, loss angle or loss tangent (tan δ). The dissipation factor is a measure of capacitor efficiency that represents the relative expenditure of energy to obtain a given amount of charge storage (Hench and West, 1990). Dielectric loss is the result of continually reversing the polarity of electric field through the dielectric material. Each time the molecular structure of the dielectric materials has to adjust a new polarity, a little electric energy will be converted into heat energy (Fowler, 1994). The dissipation factor is also

influenced by a few mechanisms such as ion migration, ion vibration and ion deformation all of which are strongly affected by the temperature and frequency (Gao and Nigel, 1999).

Since the capacitors are made from different materials, the tan δ can be used to characterize the dielectric material. Some energy is lost in real capacitors. These losses may be due to resistance losses or dielectric losses (Kingery et al., 1976). Resistance losses are electrical energy transferred to heat due to current flowing through the leads and plates of the capacitor. Dielectric losses occur due to heat produced during the change in the molecular structure of the dielectric due to the changes in polarity (Fowler, 1994).

The tan δ shows the dielectric performance via energy loss. A lower tan δ yields a better capacitor and the tan δ is measured as a percent. For a loss (imperfect) dielectric the ε_r can be represented by a complex relative ε_r in Equation (2.5):

$$\varepsilon = \varepsilon' - i\varepsilon'' \qquad (2.5)$$

The small difference in phase from ideal behavior is defined by an angle δ, defined through the Equation (2.6):

$$\frac{\varepsilon''}{\varepsilon'} = \tan\delta \qquad (2.6)$$

where, $\tan\delta$ = the loss tangent or dissipation factor

ε'' = the loss factor

Loss tangent can be used to determine the capacitor quality. The loss tangent is also used to measure the efficiency of the capacitor and the "Q" or quality factor is the reciprocal of loss tangent and is sometimes used to describe the dielectric's characteristics.

2.5 Polarization Mechanism

The basic model of polarization within the dielectric material is used to explain the increase in capacitance or ε_r. Polarization is the arrangement of induced atomic or molecular dipole moments with the help of external applied field. There are three kinds of polarization, electronic polarization, ionic polarization and orientation polarization. Usually, dielectric materials show at least one of these types which also depend on the material and the manner of externally applied field (Callister, 2007).

Electronic polarization occurs when the center of negative charged electron cloud is shifted in relation to the positive atom nucleus by the electric field Figure 2.3 (a). This phenomenon exists when electric field is present and can be found in all dielectric materials. Meanwhile, ionic polarization happens when applied field tends to shift cations and anions in opposite directions which will increase a net dipole moment. As shown in Figure 2.3 (b), this phenomenon occurs only in ionic materials (Ye, 2008).

Figure 2.3 (c) shows the orientation polarization. Orientation polarization is related to the existence of permanent electric dipoles which are present even in the absence of an electric field (Callister, 2007). The sum of these three types of polarization is equal to the total polarization P of a material which is shown in Equation (2.7). But,

probably one or more of these polarizations to be absent for total magnitude polarization is also possible (Callister, 2007).

$$P = P_e + P_i + P_o \qquad (2.7)$$

where P_e is electronic polarization, P_i is ionic polarization and P_o is orientation polarization.

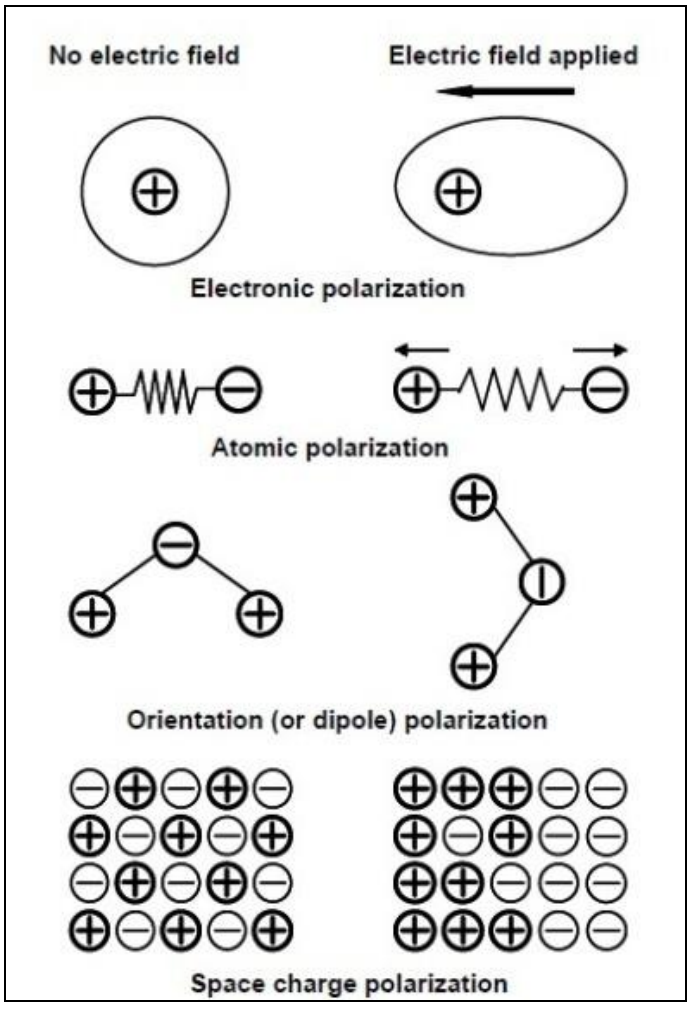

Figure 2.3: Schematic representation of different mechanism of polarization (a) Electronic polarization (b) Ionic polarization (c) Orientation polarization (Callister, 2007).

2.6 Frequency Dependence on the Dielectric Constant

Relaxation frequency is the reciprocal of the minimum reorientation time for an electric dipole within the alternating electric field (Callister, 2007) and it is determined when there are abrupt drops of the ε_r (Podpirka et al., 2012). A dipole cannot keep shifting orientation directions when the frequencies of the electric field exceed its relation frequency. So, it will not make a contribution to the ε_r. As shown in Figure 2.4, the dependence ε_r, on the field frequency exhibits all three types of polarization. When a polarization mechanism ceases to function, there is an abrupt drop in the ε_r. Otherwise, ε_r is virtually frequency independent (Callister, 2007).

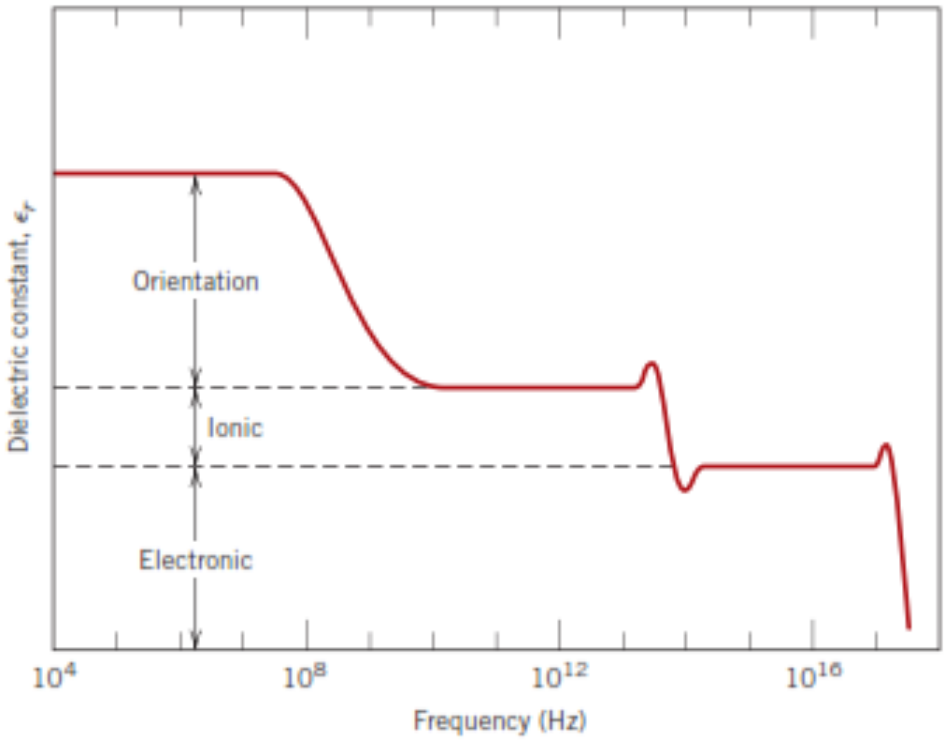

Figure 2.4: Variation of dielectric constant with the frequency of an alternating dielectric field (Callister, 2007).

If a dielectric material is subjected to polarization by an ac electric field, the dipoles attempt to reorient with the field for each reversal which requires some finite time. Some minimum reorientation time exists for each polarization type and relaxation frequency is taken as the reciprocal of this minimum reorientation time.

2.7 Nickel Oxide, NiO

NiO is a Mott-Hubbard anti-ferromagnetic insulator which crystallizes in rock salt structure (Manna et al., 2008). It is an interesting material due to its complex band structure (Gokul et al., 2013).

NiO is classified as an insulator at room temperature and an optically measured gap of 4eV (Lin et al., 2006). The optical transition giving rise to the gap absorption is in simple terms called a charge transfer transition, meaning that an electron is transferred from the oxygen valence band into the empty 3d conduction band (Hufner et al., 1992).

NiO being an ionic crystal, has the formula of Ni^{2+} and O^{2-}. NiO is a p-type semiconductor due to vacancies at Ni^{2+} sites. Figure 2.5 shows the structure of NiO consists of sheets of Ni^{2+} parallel to the (111) plane with opposite spin direction in neighbouring sheets (Mallick et al., 2009). Like many other binary metal oxides, NiO is often non-stoichiometric, meaning that the Ni:O ratio deviates from 1:1. In nickel oxide, this non-stoichiometry is accompanied by color changes, with the stoichiometrically NiO green and the non-stoichiometric NiO black (Podprika, 2012).

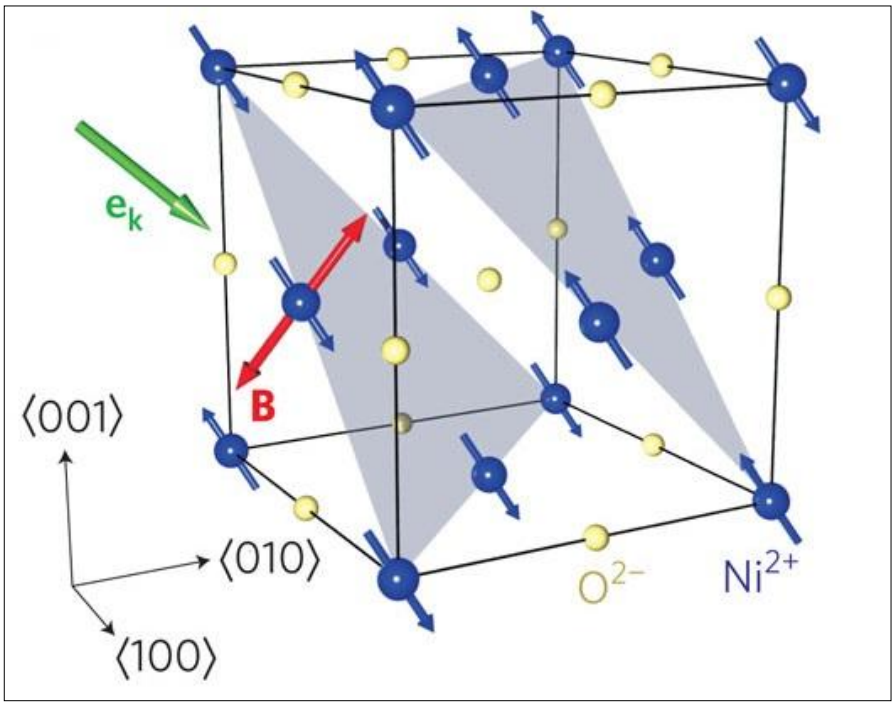

Figure 2.5: Structure of NiO with plane (111) sheets (oxygen atoms are not shown).

Figure 2.6 shows rock salt structure where anions (X) form the cation sub lattice with FCC structure and cations (M) fill the octahedral sites. It also shows 100% occupancy of sites according to the stoichiometry since there will be one octahedral site per anion. For rock salt structure, such as NaCl, MgO, NiO and FeO, the radius ratio range is between 0.414 - 0.732.

The transport mechanism of NiO has been the focus of attention at temperatures 500ºC and below. The defect structure is an important phenomenon in temperatures over 1000ºC. At high temperatures, the defect structure of NiO is still questionable, although it is generally considered to be a metal deficit, p-type semi-conductor. At high temperatures the usual reactions of equilibration occur, which are considered in NiO. NiO has attracted great attention of researchers due to its unusual

dielectric property. It exhibits large ε_r (~10^4) at room temperature and almost constantly keeps it at low frequencies over the wide temperature range from (100 to 400) K.

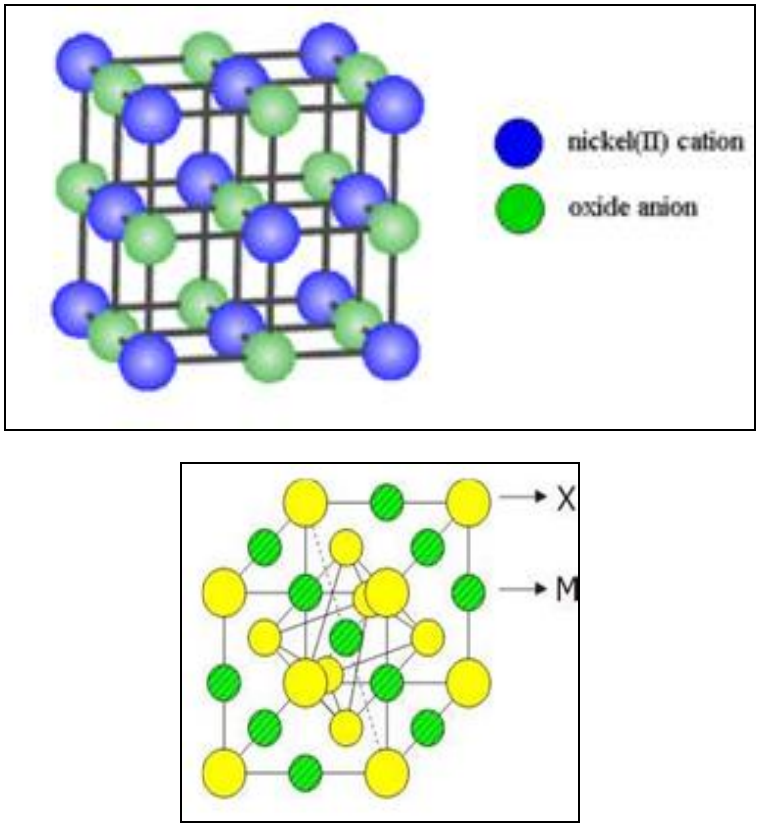

Figure 2.6: Structure of Rocksalt NiO compounds.

NiO has a defect structure with some metal ions missing. The defects can be divided into a variety of categories such as point defects, line defects and surface defects. These defects play an important role in determining the properties of ceramic materials and in this context, the role of point defects is extremely important.

Point defects are caused due to deviations from the perfect atomic arrangement or stoichiometry. These could be missing lattice ions from their positions, interstitial ions or substitutional ions (or impurities), valence electrons and/or holes. Usually, point

defects in metals are electrically neutral whereas in ionic oxides, these are electrically charged. Ionic defects occupy the lattice positions. It can be either of vacancies, interstitial ions, impurities or substitutional ions.

Meanwhile electronic defects are deviations from a ground state electron orbital configuration which give rise to such defects when valence electrons are excited into higher energy levels and lead to formation of electron or holes. The deviation from the exact stoichiometric composition is directly related to the presence of point defects. While complimentary point defects are formed in stoichiometric crystals, the electrical neutrality of nonstoichiometric compounds is conserved through the formation of point defects and complimentary electronic defects. Nonstoichiometric oxides may depend on the oxide, temperature and activities of the components which have an excess or deficit of metal or oxygen.

Nonstoichiometric oxides may be divided into four limiting groups. The first are metal deficient oxides, such as $M_{1-y}O$, where O is oxygen interstitial, M is metal interstitial, y is usually a small fraction. Metal vacancies or complex defects based on metal vacancies are the majority defects, and examples with oxides with metal deficit are $Co_{1-y}O$, $Ni_{1-y}O$, and $Fe_{1-y}O$.

Secondly are metal excess oxides, such as $M_{1+y}O$, in which metal interstitials are the prevalent defects. $Cd_{1+y}O$ is an example of an oxide with this type of nonstoichiometry. Third are metal oxygen deficient oxides, such as MO_{2-y}. In these oxides oxygen vacancies prevail and examples of such oxides are CeO_{2-y} and other

oxides with the fluorite structure. Last are oxygen excess oxides, such as MO_{2+y}. Oxygen interstitials or complex defects based on these are the predominating defects.

Although a particular type of defect predominates in an oxide and as such constitutes the majority defect in the crystal, it is important to emphasize that the crystal will contain all other defects in varying concentrations in the form of minority defects. Furthermore, the majority of defects in the crystal may also change with temperature or activity of the components in the crystal. In an oxide MO_2 the predominant defects may in principle change from oxygen vacancies to interstitial metal ions on changing the oxygen activity, and under these conditions the nonstoichiometry may be written $M_{1+x}O_{2-x}$.

The role of dopant is important but different dopants may not have the same effect on trapping electrons and holes on the surface or during interface charge transfer because of the different positions of dopant into the host lattice. It has been reported that addition of Li and Ti can improve the ε_r of the materials (Maensiri et al., 2007). The addition of Al_2O_3 decreases the tan δ and is attributed to the grain growth. Another study done by Hsiao et al. (2007) reported that addition of 5 mol% Ta_2O_5 can also increase dielectric properties. For all dopants, the grain growth occurred. Instead of ε_r increament, small amounts of doping also lead to an increase in the density and grain growth (Wu et al., 2002). However, higher amount of dopants (>10 mol %) may reduce the NiO. The Li and Li,V substitutions give an effect on the NiO microstructure and improve the ε_r due to the stabilization of the ordering induced domain boundaries via the partial segregation of cations (Hufner et al.,1992), (Pongha et al., 2009).