UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND DIELECTRIC PROPERTIES OF Bi3.36Mg1.92-xAxNb2.72O13.76 (A = Ca, Sr AND Ba) PYROCHLORE SYSTEMS

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November 2017

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Bismuth magnesium niobate (BMN) pyrochlores are one of the potential dielectrics owing to their excellent dielectric properties, e.g. high relative permittivity, ε' > 160, low dielectric loss, tan δ in the order of ~10^{-4} and compositional tunable temperature coefficient of capacitance, TCC. In this work, alkaline earth metals namely, Ca, Sr and Ba were successfully introduced into BMN pyrochlores through solid-state reaction. These substitutional solid solutions were prepared with the proposed chemical formula, $(Bi_{3.36}Mg_{0.64-x}A_x)(Mg_{1.28}Nb_{2.72})O_{13.76}$, in which the formation mechanism requires a one-to-one replacement of Mg^{2+} by A^{2+} (A^{2+} = Ca, Sr and Ba) at the eight-coordinated A site. The solid solution limits of $(Bi_{3.36}Mg_{0.64-x}A_x)(Mg_{1.28}Nb_{2.72})O_{13.76}$ are found to be $0 \le x \le 0.7$, $0 \le x \le 0.5$ and $0 \le x \le 0.2$ in the Ca-, Sr- and Ba-series, respectively. Ca-doped BMN pyrochlores have a relatively extensive solid solution limit due to the closely similar ionic radii between Ca^{2+} and Bi^{3+} with their values of 1.12 Å and 1.13 Å, respectively. These materials adopted a cubic symmetry, space group Fd3m (No. 277), Z = 4, with their refined lattice parameters, $a = b = c$, decrease linearly from 10.5968(16) Å to 10.5332(14) Å, 10.5671(17) Å and 10.5879(3) Å, respectively. On the other hand, all BMCN, BMSN and BMBN pyrochlores are found to be thermally stable as thermal event is absent within the studied temperature range ~30−1000 °C. Whilst, the irregular shaped grains of surface morphologies of these samples showing a broad distribution of mean grain size with increasing of dopant concentration. Six IR-active phonon modes are observed in these chemically doped pyrochlores, which are due to the vibration and bending of metal-oxygen bond in the range 1000 cm^{-1}−200 cm^{-1}.

All the doped BMN pyrochlores appeared to be highly insulating with their conductivities in the order of ~10^{-6}−10^{-5} Scm^{-1} at ~600 °C. These materials exhibited moderate high ε', low tan δ in the order of 10^{-3}−10^{-1} at ~30 °C and negative TCC values, ~319−933 ppm/°C in the temperature range ~30−300 °C. The recorded ε' values of Ca-, Sr- and Ba-series are in the range 69−171, 90−186 and 147−183, respectively at ~30 °C and 1 MHz. The Arrhenius conductivity plots of these doped BMN pyrochlores showed linear and reversible characteristics in a heat-cool cycle. The activation energies of BMCN, BMSN and BMBN pyrochlores are found in the range

1.17−1.47 eV, 1.20−1.49 eV and 1.18−1.30 eV, respectively. The high activation energies, Ea > 1.0 eV are required for the electrical conduction, which is probably of a hopping electronic type.

In attempts to investigate the electrical properties of pyrochlores in electrolyte, further studies have been performed by using pyrochlore thin films coated on indium tin oxide (ITO) glasses using cyclic voltametry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS), respectively. Higher specific capacitance is recorded for 1-layer sample compared to 3- and 5-layer sample coated on ITO glasses in 1.0 M KCl electrolyte. The specific capacitance of 1-layer sample is found to decrease with increasing dopant concentration in respective Ca- Sr- and Ba-series. On the other hand, the cyclic voltammogram curves of all the samples showed rectangular in shape without any pseudocapacitance effect, which is a common capacitive behaviour of electrochemical supercapacitors.

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

SINTESIS DAN SIFAT DIELEKTRIK PIROKLOR DALAM SISTEM $Bi_{3.36}Mg_{1.92-x}A_xNb_{2.72}O_{13.76}$ (A = Ca, Sr DAN Ba)

Oleh

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Piroklor yang mengandungi bismut magnesium niobat (BMN) adalah salah satu daripada dielektrik yang berpotensi disebabkan oleh ciri-ciri dielektrik yang menarik. Di antara ciri-ciri tersebut adalah, pemalar dielektrik yang tinggi, ε' > 160, kehilangan dielektrik yang rendah, tan δ dalam lingkugan ~10^{-4} dan pekali suhu kapasitan yang boleh ubah mengikut komposisi, TCC. Dalam kajian ini, logam alkali bumi, iaitu, Ca, Sr dan Ba telah berjaya diganti ke dalam piroklor BMN dengan kaedah keadaan pepejal. Larutan pepejal penggantian ini disediakan dengan menggunakan formula kimia yang dicadangkan seperti berikut, $(Bi_{3.36}Mg_{0.64-x}A_x)(Mg_{1.28}Nb_{2.72})O_{13.76}$, di mana mekanisma pembentukan sistem ini memerlukan penggantian setiap Mg^{2+} dengan A^{2+} (A^{2+} = Ca, Sr dan Ba) di tapak A yang berkoordinasi lapan. Julat larutan pepejal dalam sistem $(Bi_{3.36}Mg_{0.64-x}A_x)(Mg_{1.28}Nb_{2.72})O_{13.76}$ adalah $0 \leq x \leq 0.7$, $0 \leq x \leq 0.5$ dan $0 \leq x \leq 0.2$ untuk siri Ca, Sr dan Ba. Piroklor BMN yang didop dengan Ca mempunyai julat larutan pepejal yang lebih ekstensif jika dibandingkan dengan siri Sr^{2+} dan Ba^{2+}. Ini disebabkan oleh persamaan saiz jejari ion antara Ca^{2+} dan Bi^{3+} yang hampir sama iaitu 1.12 Å dan 1.13 Å. Bahan-bahan ini menghablur dengan simetri kubik, kumpulan ruang Fd3m (No. 277), Z = 4, dengan parameter kekisi terproses, *a* = *b* = *c* yang menunjukkan penurunan secara linear dalam semua siri. Nilai penurunan tersebut adalah daripada 10.5968(16) Å kepada 10.5332(14) Å (siri Ca), 10.5671(17) Å (siri Sr) dan 10.5879(3) Å (siri Ba). Selain daripada itu, semua piroklor BMCN, BMSN dan BMBN didapati stabil kerana tidak menunjukkan sebarang peristiwa terma dalam julat suhu yang dikaji iaitu di antara ~30−1000 °C. Manakala, morfologi permukaan untuk semua sampel-sampel dalam siri Ca, Sr dan Ba telah menunjukkan butiran yang tak sekata dan taburan purata saiz butiran yang luas serta saiz yang meningkat dengan kepekatan bahan pendop. Sebanyak enam mod fonon telah dikenalpasti sebagai IR yang aktif bagi semua siri piroklor BMN yang telah didopkan. Keseluruhan mod fonon disebabkan oleh ikatan antara logam dengan oksigen yang bergetar dan membengkok dalam julat suhu 1000 cm^{-1}−200 cm^{-1}.

Semua siri piroklor BMN yang didopkan mempunyai kerintangan yang tinggi dengan kekonduksian di antara ~10^{-6}−10^{-5} Scm^{-1} pada suhu ~600 °C. Bahan-bahan ini didapati mempunyai sifat pemalar dielektrik, ε' yang sederhana tinggi, tan δ yang rendah dalam

julat 10^{-3}−10^{-1} pada suhu ~30 °C dan nilai TCC yang negatif iaitu ~319 hingga ~933 ppm/°C dalam julat suhu ~30−300 °C. Nilai ε' yang direkodkan oleh siri Ca, Sr dan Ba adalah dalam linkungan 69−171, 90−186 dan 147−183 pada suhu ~30 °C dan 1 MHz. Lakaran kekonduksian Arrhenius bagi piroklor BMN yang didopkan telah menunjukkan ciri-ciri linear dan berbalik dalam kitaran pemanasan dan penyejukan. Tenaga pengaktifan untuk piroklor BMCN, BMSN dan BMBN adalah dalam julat 1.17−1.47 eV, 1.20−1.49 eV dan 1.18−1.30 eV. Tenaga pengaktifan yang tinggi, Ea > 1.0 eV biasanya diperlukan untuk pengaliran elektrik yang disebabkan oleh mekanisma elektron lompatan.

Dalam usaha penyiasatan mengenai sifat elektrik piroklor dalam elektrolit, kajian lanjutan telah dilakukan dengan menggunakan filem nipis piroklor pada kaca oksida indium timah (ITO). Kesemua kajian ini telah dijalankan dengan menggunakan larutan elektrolit KCl yang mempunyai kepekatan 1.0 M secara kitaran voltametri (CV), cas dan nyahcas (CD) dan spektroskopi impedans elektrokimia (EIS). Kapasitan spesifik yang tinggi telah direkodkan oleh sampel yang disalutkan dengan satu lapisan pada kaca ITO jika dibandingkan dengan tiga atau lima lapisan yang menunjukkan nilai kapasitan spesifik yang lebih rendah. Nilai kapasitan spesifik yang disalutkan dengan satu lapisan sampel merosot dengan peningkatan kepekatan bahan pendop untuk kesemua siri Ca, Sr dan Ba. Selain daripada itu, semua sampel menunjukkan kitaran lengkung voltammogram yang sama iaitu berbentuk segiempat tepat tanpa sebarang kesan pseudokapasitan dan ini menunjukkan sifat kapasitif yang biasa dalam superkapasitor elektrokimia.

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I certify that a Thesis Examination Committee has met on 15 November 2017 to conduct the final examination of Nurul Aidayu bt Mat Dasin on her thesis entitled "Synthesis and Dielectric Properties of $Bi_{3.36}Mg_{1.92-x}A_xNb_{2.72}O_{13.76}$ (A = Ca, Sr and Ba) Pyrochlore Systems" 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

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

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This is to confirm that:

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3D	three dimensions
AC	alternating current
ATR	attenuated total reflectance
CD	galvanostatic charge-discharge
CRT	cathode ray tube
CV	cyclic voltammetry
DTA	differential thermal analysis
EC	electrochemical capacitor
EDS	energy dispersive spectroscopy
EIS	electrochemical impedance spectroscopy
FT-IR	fourier transform infrared spectroscopy
FTO	fluorine-doped tin oxide
FWHM	Full width at half maximum
HTCC	high temperature co-fired ceramics
ICDD	international centre for diffraction data
ICP-OES	inductive-coupled plasma optical emission spectroscopy
ITO	indium tin oxide
LTCC	low temperature co-fired ceramics
MGC	multiplayer glass-ceramics
MLC	multi-layered ceramic
MLCC	multilayer ceramic capacitor
MOD	metalorganic decomposition
ppm	parts per million
rf	radio frequency

RR	radius ratio
SC	specific capacitance
SEAD	selected electron area diffraction
SEM	scanning electron microscopy
TCC	temperature coefficient of capacitance
TCε'	temperature coefficient of permittivity
TGA	thermogravimetric analysis
W-H	Williamson and Hall
XRD	x-ray diffraction
XRF	x-ray fluorescence
θ	Bragg angle
A	area
$a, b, c, \alpha, \beta, \gamma$	lattice parameters
C	capacitance
c	velocity of light
C_b	bulk capacitance
C_{gb}	grain boundary capacitance
C_o	vacuum capacitance
d	d-spacing
d	distance
E	electric field
E_a	activation energy
eV	electron volt
I	current
K	kelvin
k_B	Boltzmann's constant

M^*	complex electric modulus
M’	real part of electric modulus
M”	imaginary part of electric modulus
n	carrier concentration
P	Polarisation
Q	charge
Q_o	vacuum charge
R	resistance
R_b	bulk resistance
tan δ	dielectric loss
V	voltage
Y^*	complex admittance
Y’	real part of admittance
Y”	imaginary part of admittance
Z^*	complex impedance
Z’	real part of impedance
Z”	the imaginary part of impedance
α	conductivity
α_c	temperature coefficient of dielectric constant
α_e	electronic polarisability
α_i	ionic polarisation
α_o	orientation polarisation
ε	strain
ε’	real part of permittivity
ε”	imaginary part of permittivity

ε_o	free space
ε_r	relative permittivity
λ	wavelength
μ	carrier mobility
τ_c	tunable temperature coefficients of capacitance
φ	phase
χ	susceptibility
ω	angular frequency

CHAPTER 1

INTRODUCTION

1.1 The Fundamental of Ceramic

Ceramic, is also recognised as *keromos* (Greek) in ancient times originating from clay of potter which is able to be fired in the temperature range of 900−1200 °C. Clay is mouldable when it is still wet and able to retain its shape after drying and firing. After experiencing a few evolutions, clay can be converted into ceramics with outstanding mechanical and electrical properties once it is fired at appropriate high temperature. In other perspective of solid description, ceramic is a polycrystalline, inorganic and non-metallic material that gains mechanical strength through firing or sintering process regardless of it is an amorphous or single crystal (Moulson and Herbert, 2003).

1.1.1 Electroceramics

The research in electroceramics has been critically driven by the great demand in technology and device applications that widely used in energy conversion and storage, health care, electronics and communication devices and automobile transportation.

A great interest and effort has been focused on the field of electroceramic over last few decades, several subclasses of electroceramics arise in parallel with the growth of technology advancement. For example, high dielectric capacitance and consistent memories of ferroelectric materials, outstanding energy storage and conversion of solid electrolyte materials, as well as environment monitoring of semiconducting oxides are prominent for a wide range of applications. The different types of electroceramics including: (i) ceramic conductors, (ii) ionic conductor, (iii) ceramic insulators, (iv) magnetic ceramics and (v) optical ceramics.

The relative mobility of electrons within a material is known as electric conductivity. Materials with the high electron mobility are called conductors. Conductive ceramics are one of the conductors and are capable to sustain their mechanical integrity at high temperature above 1500 °C. Ceramic conductors are excellent of electricity and most of these conductors are advanced ceramics materials whose properties are modified through precise control over their fabrication from powders into products. Table 1.1 shows a list of some ceramic conductor materials used in different applications (Moulson and Herbert, 2003).

Table 1.1: List of some ceramic conductor materials used in different applications (Moulson and Herbert, 2003)**.**

Application	Materials
Resistors and Electrodes	PbO, RuO_2, $BiRu_2O_7$, SnO_2
Thermistor	$BaTiO_4$
Heating element	SiC, $MoSi_2$, ZrO_2
Chemical Sensors	ZrO_2, Al_2O_3, β-Al_2O_3, SnO_2, Nasicon, TiO_2, $SrTiO_4$, etc.
Fuel cells	Y_2O_3-ZrO_2
Batteries	β-Al_2O_3, Nasicon, Lasicon
Ceramic Capacitors	$BaTiO_3$, PZT [Pb(Zr, Ti)O_2]

In ionic conductors, the current are transported by ions moving through the crystal lattice. The electrical current transports through ions in conducting liquid are called as electrolytes whereas ion conducting solids are known as solid electrolytes. The conductivity values in ionic conductors for liquid electrolyte materials and solid electrolyte materials are in the range of 10^{-1}–10^{3} Sm^{-1} and 10^{-1}–10^{3} Sm^{-1}, respectively. Whilst, the factors that influencing the conductivity values, α are (i) carrier concentration, *n*, (ii) carrier mobility, μ and (iii) charge of carriers, *Z* as formulated in equation below:

$$\alpha = nZe\mu \qquad (1.1)$$

Table 1.2: List of few conductive ceramic materials used as solid electrolytes in sensor to sense different elements and compounds (Moulson and Herbert, 2003)**.**

Solid Electrolyte	Elements/Compounds
Stabilised ZrO_2	Oxygen
Sulfur	CaS, CaF_2, β-Alumina, Nasicon
Stabilised ZrO_2, K_2SO_4, Na_2SO_4, Li_2SO_4, β-Alumina and Nasicon	SO_x (x = 2.3)
Stabilised ZrO_2	NO_x (x = 1.2)
Stabilised ZrO_2, K_2SO_4 and Na_2SO_4	CO_x (x = 1.2)

In contrast to conductors, insulators are materials that impede the free flow of electrons from atom to atom, offering very large resistance to the flow of electric current. Some materials are particularly good insulators and can be characterised by their high resistivities, e.g. glass, mica and quartz (fused) having their resistivity value of 10^{12}, 9×10^{13} and 5×10^{16} ohm m, respectively. The materials generally used for insulating purpose are called as insulating materials which have some specific properties: (i) it must be mechanically strong enough to carry tension and weight of conductors, (ii) it must have very high dielectric strength to withstand the voltage stresses in high voltage system, (iii) it must possess high insulation resistance to prevent leakage current to the earth, (iv) the insulating material must be free from undesired impurities, (v) it should not be porous, (vi) there must not be any entrance on the surface of electrical insulator so that the moisture or gases can enter in it and (vii) the physical as well as electrical properties must be less affected by changing temperature. The materials with the insulating components based on natural minerals include porcelains (clay-based and talc-based), alumina, beryllia, glass, polymer insulators, aluminium nitride and ceramic ‘packaging’ technology (Moulson and Herbert, 2003).

Over the past decade, ceramic magnets have been firmly established as electrical and electronic engineering materials; containing iron as a major constituent and are known collectively as ‘ferrites’. Ampere, Biot, Savart and Oersted were among the first to demonstrate that conductors carrying currents produced magnetic fields and exerted ‘Lorentz’ forces on each other (Barsoum, 2003). Magnetic ceramics possess excellent properties, e.g. strong magnetic coupling, low loss characteristics and high electrical resistivity and these features help to create new devices for applications in data storage, tunnel junctions, high frequency applications and spin valves. Magnetic materials can be identified based on magnetic susceptibility values. Materials with negative susceptibility (χ_m < 1) are diamagnetic which show very insignificant negative susceptibility value. Superconductor in superconducting state exhibiting χ_m = 1, which is very useful for magnetic levitation applications. However, materials with χ_m > 1 are either paramagnetic (small positive susceptibility value) or ferromagnetic (large positive susceptibility value) (Moulson and Herbert, 2003). Table 1.3 shows the different types of magnetism with the susceptibility value of some materials.

Table 1.3: Different types of magnetism with the susceptibility value of some materials (Moulson and Herbert, 2003)**.**

Type of Magnetism	Material	χ (SI) unitless	χ (cgs) unitless	μ unitless
Diamagnetic	Cu	-9.7×10^{-6}	-0.77×10^{-6}	0.99999
	Si	-4.1×10^{-6}	-0.32×10^{-6}	0.99999
Paramagnetic	Al	$+20.7\times10^{-6}$	$+1.65\times10^{-6}$	1.00002
	Pt	$+264.4\times10^{-6}$	$+21.04\times10^{-6}$	1.000026
Ferromagnetic	Low carbon steel	$\approx5\times10^{3}$	3.98×10^{2}	5×10^{3}
	Fe-3%Si (Grain Oriented)	4×10^{3}	3.18×10^{3}	4×10^{4}

Diamagnetic materials are materials having electron motions in the way of those electrons produce net zero magnetic moment in the absence of any magnetic field (Goldman, 2006).

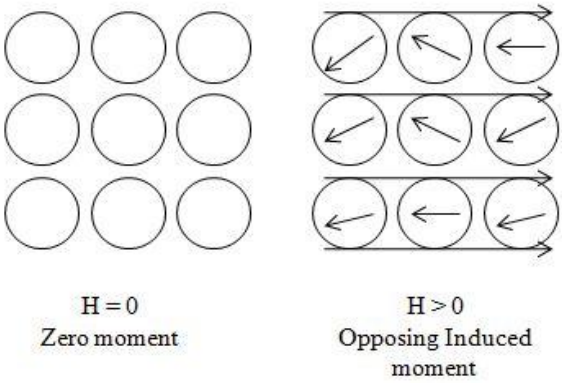

Figure 1.1: Description of a diamagnetic material in the absence of a magnetic field and when a field is applied (Goldman, 2006)**.**

In paramagnetic materials, atoms possess a permanent non-zero net magnetic moment owing to factor of orbital and spin magnetic moments. However, once magnetic field is applied, magnetic moment would align up in the direction of magnetic field overcoming thermal barrier and creating a positive magnetic moment with small susceptibilities, 10^{-3} to 10^{-6} (Riedel and Chen, 2014).

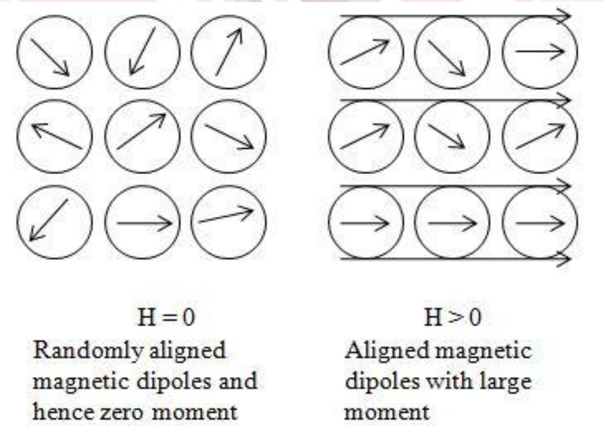

Figure 1.2: Schematic diagram of spins in a paramagnetic solid (Riedel and Chen, 2014)**.**

Ferromagnetic materials are quite similar to paramagnetic materials in term of having permanent magnetic moment, but ferromagnetic materials have its regions or domains in ordered and aligned that give rise to large finite magnetisation in the absence of magnetic field. When magnetic field is applied, ferromagnetic materials exhibit a ferroelectric-like hysteresis loop between magnetisation and magnetic field as below.

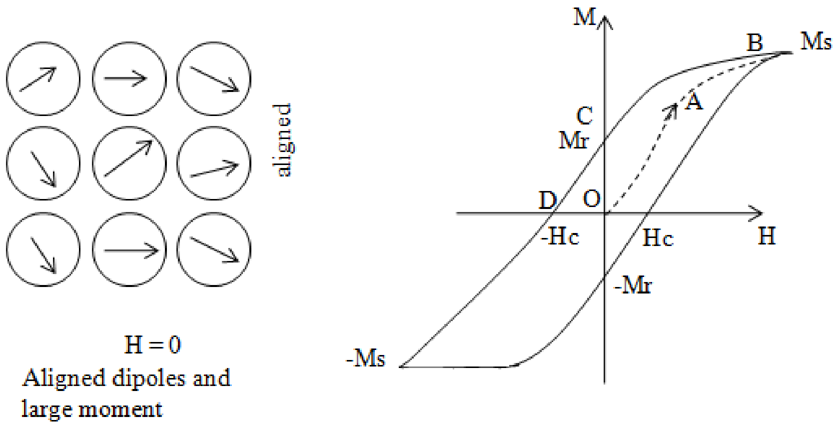

Figure 1.3: Schematic diagram of spins in a ferromagnetic material and ferromagnetic hysteresis loops (Riedel and Chen, 2014)**.**

Optical ceramics, also known as transparent ceramics is a great substitution of single crystal due to several reasons, e.g. cost effectiveness, large-scale production, feasibility of shape controlling and better mechanical properties. Unlike single crystal, transparent ceramics have various sites to scatter light, e.g. residual pores within grains and grain boundaries, grain boundaries, second phase at the grain boundaries and double refraction from birefringent materials. The most critical factor for transparency of the ceramics is porosity. The presence of a large number of pores makes the ceramic opaque (non-transparent). Transparent ceramics contain both grains and grain boundaries. If there is a deviation in properties such as composition between grains and grain boundaries, the interfaces between them would be the scattering sites of light. Thus, the difference in optical characteristic between grains and grain boundaries should be minimised in order to keep ceramic transparent (Kong *et al.*, 2015). For example, the transparent ceramics, α-alumina (Al_2O_3) or addressed as corundum is the only thermodynamically stable crystallographic modification of alumina. Corundum has its O^{2-} ions arranged in hexagonal arrangement with Al^{3+} occupying two-thirds of the octahedral interstitial position in hexagonal crystal lattice. Corundum exhibits maleficent properties, e.g. high strength, high hardness, and excellent corrosive resistance, making corundum a promising and favourable candidate for applications in electromagnetic windows, transparent armor and envelops of high pressure metal halide lamps (Kong *et al.*, 2015).

In the near future, electroceramic materials will be a favourable choice to be intensively integrated in many ways of virtual design to fit into this evolution especially through miniaturisation of conventional semiconducting, superconducting and ironically conducting materials without losing or degrading the potential properties (Setter and Waser, 2000).

1.2 Dielectric Materials

Dielectrics or electrically insulated materials are defined as a class of materials in which electrostatic fields could hold for a long time, offering a very high resistance to electric current flow. Thus, dielectrics materials are always a favourable choice of a wide spectrum of applications including devices of energy storage in capacitors, charge storage in photosensitive materials of printers and copying machines, transducers in condenser and piezoelectric microphone, liquid crystals for alphanumeric displays and other display usages (Murarka *et al*., 2003; Ho *et al*., 2002).

Dielectric materials typically are not utilised to pass electrical energy via conduction, yet they could become a media transferring electrical energy through displacement of current. Distinction of dielectric properties depending on composition, structure and experimental condition of the dielectric materials has been established since these are the key factors to be altered in order to satisfy the needs of different applications and to enhance the performance and reliability of dielectric materials. Thus, various dielectric properties are carefully deliberated especially the ability of reservation and dissipation of electric and magnetic energies, and degree of polarisation, magnetisation and conduction (Jack and George, 1979).

1.2.1 Dielectric Constant

Dielectric constant, also addressed as relative permittivity, ε', is one of the chief factors to be regarded in designing the performance of dielectric material during practical applications. Dielectric constant defines the ability of material to concentrate electrostatic flux or to store electrical energy in the presence of an electric field (Bartnikas, 1987).

There are a few categories of dielectric material depending on the magnitude of dielectric constant, which are low, medium and high permittivity classes. High permittivity dielectric materials, e.g. $BaTiO_3$ could be a great substitution for mica in capacitors. Meanwhile, titanium oxide could be used to modify medium and low permittivity classes especially for the low-loss stable capacitors and microwave capacitors. The ceramic insulators include silicates and aluminas that used to be utilised as ceramic insulating purposes (Nanni *et al*., 1999).

Dielectric constant can be described as a comparison between permittivity of a medium and permittivity of free space as formulated below:

$$\varepsilon_r = \varepsilon/\varepsilon_o \qquad (1.2)$$

All materials, inclusive vacuum, do store energy when electric field applied. The permittivity of free space, ε_o is a constant with value $\varepsilon_o = 8.854\times10^{-12}$ Fm^{-1}. Apparently, capacitor materials are not all originated from free space, thus ε is the absolute permittivity of a medium and ε_r is the relative permittivity which has a value always greater than 1, representing all materials are able to store more electrical energy than free space in the presence of electric field (Nalwa, 1999).

1.2.1.1 Polarisations

When a potential difference, V is applied between two parallel electrodes that having an area of cross section, A m^2 and distance, d m apart in a vacuum capacitor, the electric field, E between the electrodes perpendicular to the plates, regardless edge effect, (Raju, 2009).

$$E = V / d \quad (1.3)$$

Thus, the capacitance of vacuum capacitor is:

$$C_o = \varepsilon_o A / d \quad (1.4)$$

Moreover, charge captured in the vacuum capacitor is then becomes:

$$Q_o = \varepsilon_o AE \quad (1.5)$$

where ε_o is the permittivity of free space.

Homogenous dielectric leads to potential constant, and charge stored is then formulated as:

$$Q = \varepsilon_o \varepsilon AE \quad (1.6)$$

where ε is the dielectric constant of the material (permittivity of the medium).

Apparently, ε is always greater than unity and Q is greater than Q_o, a raise in charge stored due to appearance of charges on the dielectric surface, is described as:

$$Q - Q_o = AE\varepsilon_o (\varepsilon - 1) \quad (1.7)$$

If charges in the system are neutral, dipole moment is created as:

$$\mu = AE\varepsilon_o (\varepsilon - 1)\, d \quad (1.8)$$

Since volume of dielectric is v = Ad, then dipole moment per unit volume is:

$$\mu / Ad = E\varepsilon_o (\varepsilon - 1) \quad (1.9)$$

Polarisation, P is defined as the dipole moment per unit volume and expressed as:

$$P = E\varepsilon_o (\varepsilon - 1) \tag{1.10}$$

$$P = \chi E\varepsilon_o \tag{1.11}$$

where χ is $(\varepsilon - 1)$ which is known as susceptibility of medium.

In short, polarisation is defined as a vector quantity of the dielectric dipole moment per unit volume regarding magnitude and direction. Yet, polarisation is charge per unit area on the surface of dielectric material in the absence of electric field (Kim and Tadokoro, 2007).

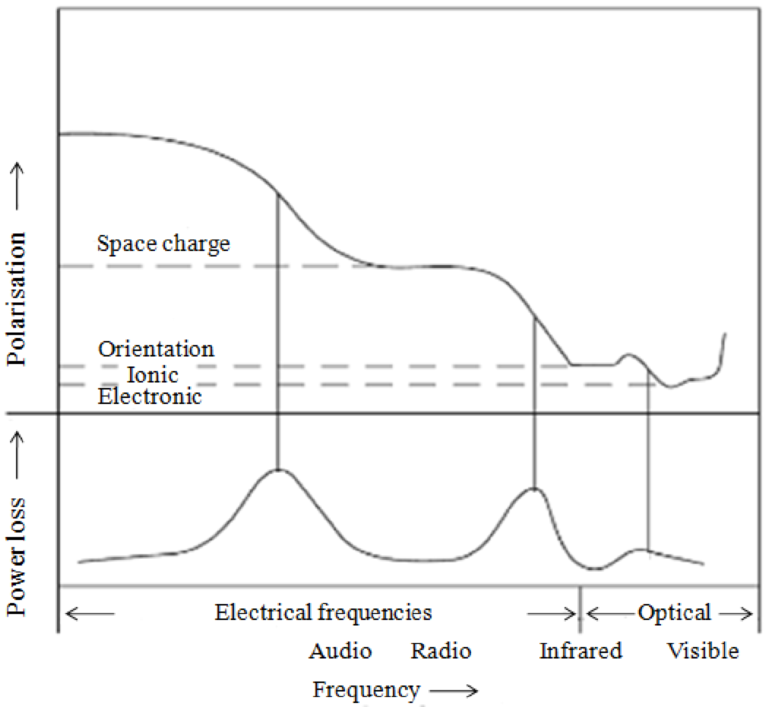

Figure 1.4: Frequency dependence of polarisation processes and peak power losses (Kim and Tadokoro, 2007)**.**

1.2.1.1.1 Electronic Polarisation

In the existence of external electric field, a slightly displacement occurs between positive charged nucleus and negative electron cloud in the way of positive charged nucleus stays in direction of electric field and negative electron cloud sits in opposite direction, Consequently, positive nucleus is no longer at centroid of electronic charge, thus resulting electronic polarisation. Electronic polarisation has a small magnitude of polarisation because the external electric field applied is usually weak compared with intra-atomic field (Kim and Tadokoro, 2007).

Electronic polarisation is proportional to the magnitude of field strength formulated as below:

$$P_e = \alpha_e E \tag{1.12}$$

where α_e is the electronic polarisability constant in which α_e increases when atom becomes larger, and α_e is independent of temperature since electronic structure of an atom is insensitive towards temperature. In addition, α_e is also independent of frequency due to electronic polarisation occurs within extremely short time (~10^{-15} to ~10^{-14} seconds).

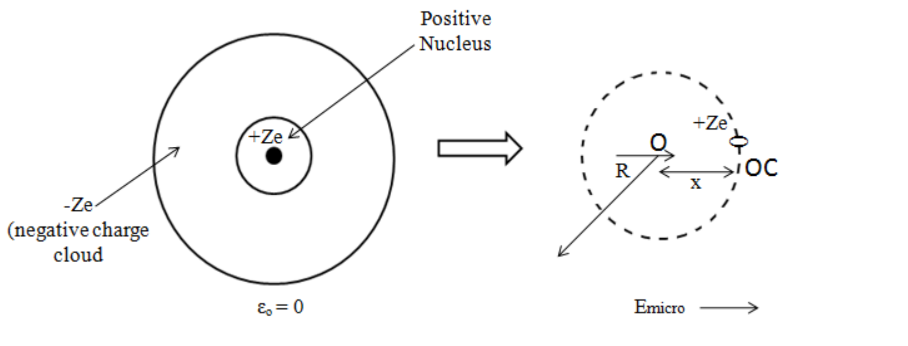

Figure 1.5: The total negative charge -Ze is distributed homogenously throughout the sphere of R (a) while the nucleus and electron cloud are displaced in opposite direction (b) (Maheshwari, 2006)**.**

1.2.1.1.2 Ionic Polarisation

Ionic polarisation happens owing to displacement of the atomic components of the molecule in electric field when atoms transform to molecules. During the transformation to molecules, electron clouds of atoms do not distribute their electron symmetrically or evenly since electron clouds tend to stay towards atoms with higher electronegativity. Thus, molecules formation requires atoms with charges of opposite polarity. With application of external electric field, net charges alter the equilibrium position of atoms themselves, resulting ionic polarisation which has a smaller polarisation magnitude, approximately one-tenth of electronic polarisation (Gnaneswara-Rao, 2008; Marikani, 2017).

$$P_i = \alpha_i E \tag{1.13}$$

where α_i is the ionic polarisation constant in which $\alpha_i = 0.1\alpha_e$ due to greater mass of ions (~10^{-13}), and α_i is independent of temperature because molecular structure and electron distribution in molecule are insensitive of both temperature and frequency.

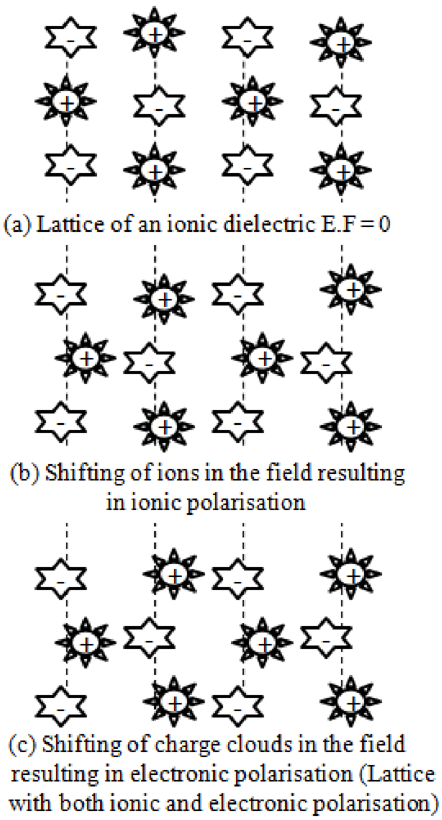

Figure 1.6: Ionic polarisation measures shift of ions relative to each other and electronic polarisation measures shift of electron cloud relative to nucleus within the atom (Maheshwari, 2006)**.**

1.2.1.1.3 Orientational Polarisation

Organic molecules, e.g. CH_3Cl, H_2O and HCl in general have significant difference in electronegativity between the positive and negative partial charge and this could create dipoles moment in the absence of electric field. Dipole moment shown is negligibly small since molecules dipoles are oriented randomly without existence of electric field. With the aid of electric field, orientation of dipoles is arranged in the direction of electric field resulting in vast dipole moments (Mitchell, 2004; Marikani, 2017).

$$P_o = \alpha_o E \tag{1.14}$$

where α_o is the orientation polarisation constant in which α_o is dependent on temperature and α_o decreases with increase in temperature due to thermal energy of high temperature is able to disorient the dipoles.

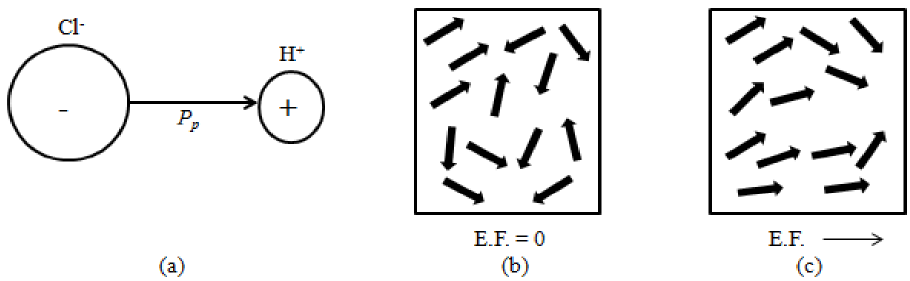

Figure 1.7: Orientation polarisation produced in the case of a polar molecule of an electric field (Maheshwari, 2006)**.**

1.2.1.1.4 Space Charge Polarisation

Charge carriers commonly exist in heterogeneous systems where charge carriers can migrate through material under the effect of external electric field. However, when the charge carriers have its motion obstructed, charge carriers are confined at defect sites or at interface between medium that have dissimilar dielectric constant and conductivity, thus hindering the movement of charge carriers in discharging or replacing at the electrodes. Consequently, inhibition of charge carrier movement leads to space charge of macroscopic field distortion (Martin *et al*., 2009; Macdonald, 1953).

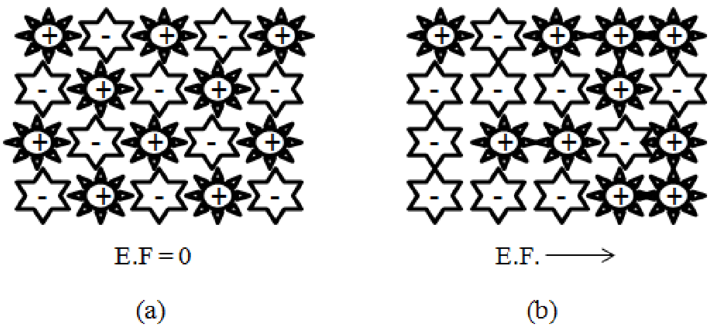

Figure 1.8: Space charge polarisation (Maheshwari, 2006)**.**

1.2.2 Dielectric Loss

Dielectric loss, or dissipation factor is meant to display deviation from ideal behavior of a dielectric material, or defined as quantitatively dissipation of the electrical energy due to various physical processes, e.g. electrical conduction, dielectric relaxation, dielectric resonance and losses besides a typical loss comes from a delay between electric field and electric displacement vector (Sawada *et al.*, 1999). Dielectric loss can be branched into intrinsic and extrinsic loss. Intrinsic losses are the losses in a perfect crystal depending on the crystal structure, and significantly due to dielectric relaxation in ideal lattice at low frequency that leads to release of heat. Extrinsic losses are attributed by imperfections in a crystal structure due to the presence of impurities, microstructural defects, porosity, grain boundaries, dislocations and vacancies (Sebastian, 2008).

$$\tan \delta = \varepsilon''/\varepsilon' \qquad (1.15)$$

The equation above illustrates ratio of the imaginary permittivities to the real storage relative permittivities or can also be explained as ratio of the energy dissipated to energy stored in material. The tangent of the loss angle is present when a dielectric is susceptible to a sinusoidally varying applied electric field. Ordinarily, dielectric loss is determined experimentally using same method as the procedure used to find dielectric constant concurrently. Dielectric loss is affected by temperature and frequency, until a maximum value of dielectric relaxation is overcame (Alger, 1997).

1.2.3 Temperature Coefficient of Capacitance (TCC)

Temperature coefficient of capacitance (TCC) is the maximum change in capacitance over a specific temperature range. The capacitance value stated by the manufacturer is established at a reference temperature range of ~30 °C to ~300 °C. TCC should always be considered for applications operating above or below this temperature. For class I capacitors, they are highly stable with temperature and are referred to as temperature compensating. It is always specified as the capacitance change in parts per million (ppm) per degrees centigrade, and the maximum capacitance change is calculated via formula below:

$$TCC = (C_f - C_i)\ 1{,}000{,}000 / (T_f - T_i)\ C_i \qquad (1.16)$$

where C_f and C_i is the capacitance value at initial temperature, T_i (~30 °C) and final temperature T_f (~300 °C) respectively.

Meanwhile, for class II capacitors, it is different from class I which is not the temperature stable but having the main advantage in volumetric efficiency, e.g. in the case involving more capacitance. This capacitors are best suited for applications where higher capacitance values are important while charge *Q* and stability over temperature are not of major concern. Temperature coefficient of capacitance for class II capacitor dielectrics are expressed as a percentage. TCC should always be operating at temperature above or below 25 °C (Fiore, 2000).

1.3 Applications of Dielectric Ceramics

1.3.1 Low Temperature Co-fired Ceramics (LTCC)

Material made up of low fraction of dielectric ceramic (3/1), is known as low temperature co-fired ceramics (LTCC) or can be called as multiplayer glass-ceramics (MGC). LTCC material can be sintered at much lower firing temperature (850 ºC to 900 ºC) compared to high temperature co-fired ceramics (HTCC) that is sintered at high temperature around 1500 ºC. Since LTCC can be produced at much lower temperature, low resistivity precious metal conductors, e.g. gold and silver can be used as the cathode materials of LTCC material to suit many electrical applications.

To satisfy the demand for new packaging technology that requires high frequency and high interconnect density material, new glass-ceramic materials with low dielectric constant are highly needed. Unlike alumina with high dielectric constant that is able to give a trouble in switching speed, silver and palladium in desired particle shape are preferred and needed as glass-ceramic substrate to fulfil the latest technology requirements: (i) new LTCC material with an insignificant propagation delay due to low dielectric constant material and (ii) low electrical resistivity and low cost of improved electrical design that helps to control characteristic impedance and crosstalk coupling noise (Christou, 2006).

Table 1.4: Typical materials of low and high temperature co-fired ceramic systems (Christou, 2006)**.**

	Ceramics		Conductor	
	Material	Firing temperature (°C)	Material	Melting point (°C)
LTCC	• Glass/Ceramic composite • Crystallised glass • Crystallised glass/Ceramic composite • Liquid-phase sintered ceramics	900 to 1000	Cu Au Ag Ag-Pd Ag-Pt	1083 1063 960 960-1555 960-1186
HTCC	• Alumina ceramics	1600 to 1800	Mo W Mo-Mn	2610 3410 1246-1500

1.3.2 Multilayer Ceramic Capacitors (MLCC)

Recently, ceramic capacitor has achieved the highest number in production and sales among fine ceramics products in a rapidly growth market. Multilayer ceramic capacitor (MLCC) has its demand raises remarkably year by year and reaches global output demand as high as 9 trillion units. The advancement of technology does not halt by just here, stringent requirements that demand high specific capacitance, high layer number with ultra-thin layer and cost effectiveness in the production. MLCCs can be found widely in applications ranging from military, spaceflight, communication to national defence (Yin *et al*., 2009). In the trend of miniaturisation of ceramic capacitors, MLCC layers are reduced from 10 μm to 3 μm and towards 1 μm. Thus, MLCC ceramic grain size has to be controlled within nanoscale of 100 nm suggesting that grain growth needs to be suppressed during sintering process.

1.4 Problem Statements

It is imperative to prepare novel pyrochlores with excellent electrical performance especially the complex family of pyrochlores has a wide range of compositions and electrical properties. By far, bismuth zinc niobate pyrochlores (BZN) and bismuth magnesium niobate pyrochlores (BMN) are well known to be used as dielectric materials that are applicable for technological devices and modules. Thus, the preparation of new BMN pyrochlore through chemical doping is expected to yield materials with high dielectric constant and low dielectric loss. The selection of these dopants is due to the reasons including: (i) larger ionic radius that suits the requirement of relatively larger A site, (ii) same oxidation state with Mg^{2+} and (iii) high polarisability of Ca^{2+}, Sr^{2+} and Ba^{2+}, which is expected to enhance the dielectric properties. The idea of depositing Ca, Sr and Ba doped BMN pyrochlores on thin film in solid electrolyte systems by using electrochemical impedance spectroscopy method (EIS) is due to their vast applications as energy storage devices for electronic components, electric vehicles and memory back-up systems in mobile phone and computers. Utilisation of this technique has attracted the attention of worldwide researchers due to their excellent specific capacitance, e.g. ~59 F/g and 123.8 F/g (Chang *et al*., 2012b; Chee *et al*., 2015) with a good electrochemical stability. By far, information and literature concerning the properties of pyrochlores in the doped BMN systems are rarely found. Therefore, control of composition, synthesis condition and chemical dopants is of utmost importance in order to synthesise new pyrochlores with improved electrical properties.

1.5 Objectives

The objectives of this research are:

i. To prepare chemically doped pyrochlores in the Bi_2O_3-MgO-AO-Nb_2O_5 (A = Ca, Sr and Ba) ternary systems.

ii. To study structural and thermal properties of the prepared pyrochlores.

iii. To characterise the electrical behavior of the chemically doped BMN pyrochlores by AC impedance spectroscopy.

iv. To investigate specific capacitance of pyrochlore thin films coated on indium tin oxide (ITO) glass using electrochemical impedance spectroscopy method (EIS).

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