

CHAPTER III

EXPERIMENTAL PROCEDURES

In this chapter, the experimental procedures are categorized into three main sessions. The first session deals with the chemical substances and apparatus used in this research. The second session demonstrates the preparation and processing techniques for bismuth sodium lanthanum titanate and their modified compounds. The last session is the discussion on physical techniques and electrical measurements.

3.1 Chemical Substances and Apparatus

The starting materials for all compositions were Bi_2O_3 , Na_2CO_3 , TiO_2 , La_2O_3 , ZrO_2 , Nb_2O_5 and Fe_2O_3 with their sources being reported in Table 3.1. All of the selected starting materials have the purity more than 99%. The as-received oxides and carbonate were characterized for the particle size distribution and thermal behavior; the results will be shown in the next chapter. The equipments and apparatus used in this research were shown in Table 3.2.

Table 3.1 The sources of raw materials used for the powder preparation

Chemical substances	Supplier's name	Formula weight (g/mol)	Purity (%)
Bismuth oxide (Bi_2O_3)	Fluka chemika	465.96	≥ 99.8
Sodium carbonate (Na_2CO_3)	Fluka chemika	105.99	≥ 99.5
Titanium oxide (TiO_2)	Alfar Asar	79.90	≥ 99.5
Lanthanum oxide (La_2O_3)	Fluka chemika	325.81	≥ 99.98
Zirconium oxide (ZrO_2)	Aldrich	123.22	≥ 99.9
Niobium oxide (Nb_2O_5)	Sigma-Aldrich	92.91	≥ 99.9
Iron oxide (Fe_2O_3)	Aldrich	159.69	≥ 99

Table 3.2 The apparatus and instruments used for this research.

Apparatus and Instrument	Company	Model
-Balance 4 digits	Satorious	BP 2215
-Polyethylene bottle	Nalgein	150 ml
-YSZ ball	Sernic	8 mm. diameter
-Ball milling machine	Pethkasem	300 rpm
-Cold Isostatic Press (CIP) Machine	Kobelco	Dr.CIP
-Oven	Memmert	UE-300
-Muffle furnace, Max. temp. 1500 °C	Lentron	-
-Verniermeter	Mitutoyo	Digimatic
-Micrometer	Mitutoyo	Digimatic
-Punch and die	-	-
-Uniaxial hydraulic press	Enerpac S.E.	SEFT-20-1
-Grinding and polishing machine	Struer	-
-Hotplate	IKA	-
-X-ray diffractometer (XRD)	Jeol	JSM-5401
-Particle size analyzer	Malvern	Mastersizer-S
-L-C-R meter	Hewlette Packard	4194A
-Hysteresis analyzer		RT66A
-Resistivity Chamber	Keithley	6150
-Simultaneous Thermal Analyzer	Netzch	STA 449
-Differential Scanning Colorimeter	Mettler Toledo	DSC822 ^e

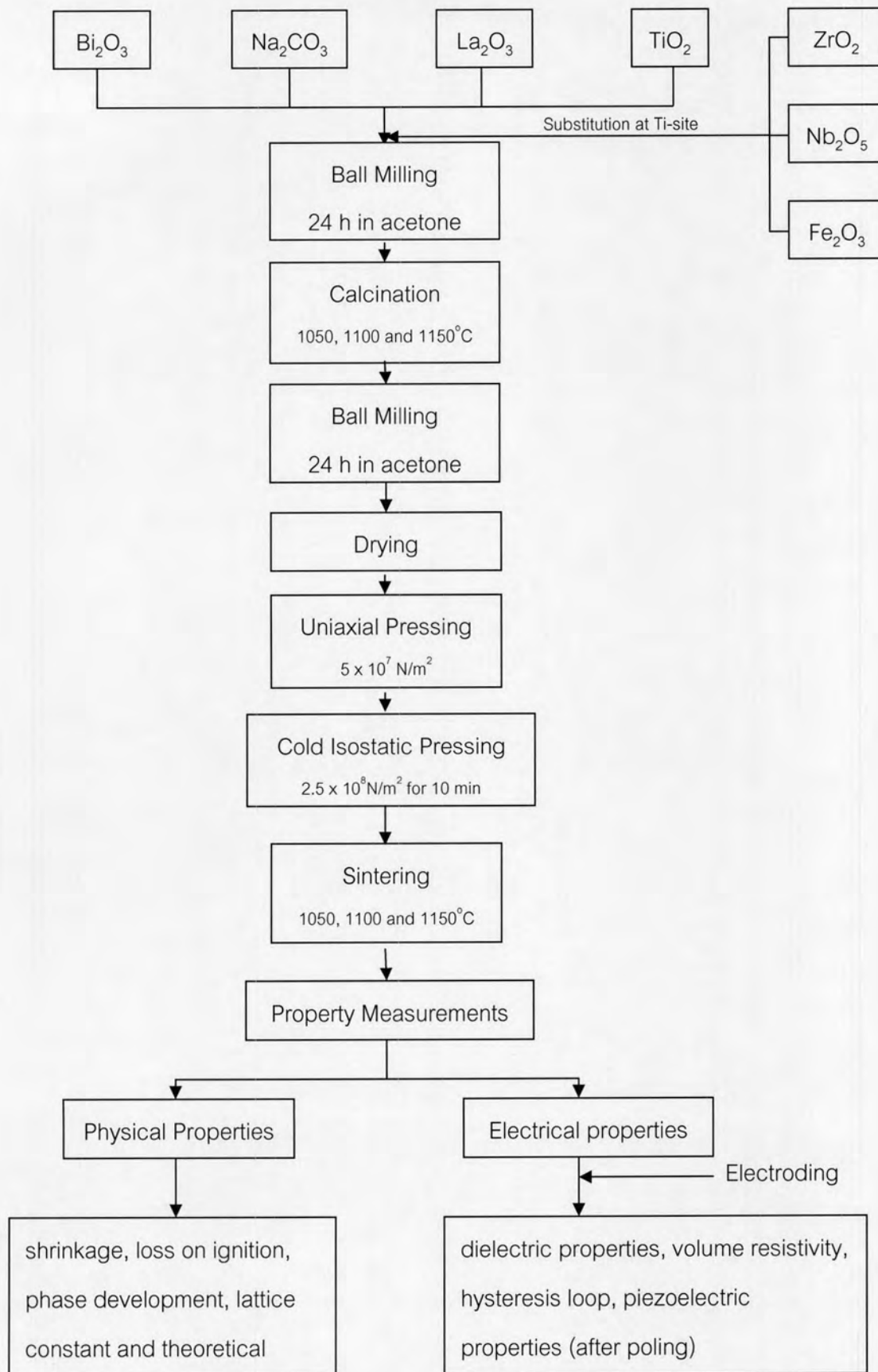


Fig. 3.1 A schematic flowchart of the conventional mixed oxide method [5].

3.2 Bismuth Sodium Titanate Ceramic Preparations and Processing

3.2.1 Chemical Compositions

The chemical compositions of the sample are categorized into three groups. The first group is a $(\text{Bi}_{0.5}\text{Na}_{0.485}\text{La}_{0.005})\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$, x is an atomic fraction at B-site cations of substituent. The second group is a $(\text{Bi}_{0.5}\text{Na}_{0.485}\text{La}_{0.005})\text{Nb}_x\text{Ti}_{(1-(5/4)x)}\text{O}_3$ and the third group is a $(\text{Bi}_{0.5}\text{Na}_{0.485}\text{La}_{0.005})\text{Fe}_x\text{Ti}_{(1-(3/4)x)}\text{O}_3$. All compositions are summarized in Table 3.3, 3.4, 3.5 and 3.6

Table 3.3 Chemical formulas of all compositions used in powder preparation

Formulas	Atomic fraction of substituents; x
$(\text{Bi}_{0.5}\text{Na}_{0.485}\text{La}_{0.005})\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$	$x = 0.005, 0.010, 0.015, 0.020$ and 0.025
$(\text{Bi}_{0.5}\text{Na}_{0.485}\text{La}_{0.005})\text{Nb}_x\text{Ti}_{(1-(5/4)x)}\text{O}_3$	$x = 0.005, 0.010, 0.015, 0.020$ and 0.025
$(\text{Bi}_{0.5}\text{Na}_{0.485}\text{La}_{0.005})\text{Fe}_x\text{Ti}_{(1-(3/4)x)}\text{O}_3$	$x = 0.005, 0.010, 0.015, 0.020$ and 0.025

Table 3.4 Chemical compositions of Zr substitution used in powder preparation

$(\text{Bi}_{0.5}\text{Na}_{0.5}\text{La}_{0.005})\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$	Weight of powder (g)					
	Bi_2O_3	Na_2CO_3	La_2O_3	TiO_2	ZrO_2	Total weight
$x = 0.5$	52.2090	11.5194	0.3651	36.6304	0.2761	100.0000
$x = 1.0$	52.1584	11.5082	0.3647	35.4170	0.5517	100.0000
$x = 1.5$	52.1078	11.4971	0.3643	35.2040	0.8268	100.0000
$x = 2.0$	52.0574	11.4859	0.3640	34.9914	1.1013	100.0000
$x = 2.5$	52.0071	11.4787	0.3636	34.7792	1.3753	100.0000

Table 3.5 Chemical compositions of Nb substitution used in powder preparation

$(\text{Bi}_{0.5}\text{Na}_{0.5}\text{La}_{0.005})\text{Nb}_x\text{Ti}_{(1-x)}\text{O}_3$	Weight of powder (g)					
	Bi_2O_3	Na_2CO_3	La_2O_3	TiO_2	Nb_2O_5	Total weight
x = 0.5	52.3146	11.5427	0.3658	35.6576	0.1194	100.0000
x = 1.0	52.3695	11.5548	0.3662	35.4706	0.2390	100.0000
x = 1.5	52.4245	11.5669	0.3666	35.2831	0.3589	100.0000
x = 2.0	52.4797	11.5791	0.3670	35.0953	0.4790	100.0000
x = 2.5	52.5350	11.5913	0.3673	34.9070	0.5994	100.0000

Table 3.6 Chemical compositions of Fe substitution used in powder preparation

$(\text{Bi}_{0.5}\text{Na}_{0.5}\text{La}_{0.005})\text{Fe}_x\text{Ti}_{(1-x)}\text{O}_3$	Weight of powder (g)					
	Bi_2O_3	Na_2CO_3	La_2O_3	TiO_2	Fe_2O_3	Total weight
x = 0.5	52.2676	11.5323	0.3655	35.7152	0.1194	100.0000
x = 1.0	52.2754	11.5340	0.3655	35.5861	0.2389	100.0000
x = 1.5	52.2833	11.5358	0.3656	35.4570	0.3584	100.0000
x = 2.0	52.2911	11.5375	0.3656	35.3278	0.4779	100.0000
x = 2.5	52.2990	11.5392	0.3657	35.1986	0.5975	100.0000

3.2.2 The BNT-based Composition Preparation

The starting materials of all compositions are Bi_2O_3 , Na_2CO_3 , La_2O_3 , TiO_2 , ZrO_2 , Nb_2O_5 and Fe_2O_3 . The preparation steps are shown by the schematic flowchart in Fig. 3.1. The oxides and carbonate were weighed in the proportions from formulas (shown in Table 3.4-6) and mixed by conventional mixed oxide method in polypropylene bottle with yttria stabilized zirconia balls sized 8 mm in diameter. The absolute acetone was used as a dispersing medium with ratio of 1:1 for the mixture of mixed powder: acetone. The milling time was 24 hrs.

After milling, the slurry was then passing through suction and drying step. The powders were calcined at three temperatures of 750, 800 and 850 °C with 100 °C/hr of heating rate and 2 hrs of soaking time. The calcined powders were milled again for 24 hrs in absolute ethanol with the weight ratio 1:1 of for calcined powder: ethanol. The slurry was then dried and sieved, and was pressed into circular pellets sized 20 mm in diameter and 1.5 mm in thickness. The green pellets were cold isostatic pressed (CIP) at $2.5 \times 10^8 \text{ N/m}^2$ to increase the green density of pellets.

The green pellets were sintered on platinum foil in air at three temperatures of 1050, 1100 and 1150 °C with 2 hrs of soaking time. The sintered pellets were polished and electroded with an air-dried silver paste, and then were dried at 50 °C in oven for 1 hr. The electroded pellets were poled by a conventional polling method.

3.3 Measurements of Physical Properties

The characterization technique was stated in this section. The way in which each technique was performed is schematically presented in Fig. 3.2.

3.3.1 Particle Size Analysis

Mastersizer basically provided a collimated He-Ne laser that passes through the sample to be measured. The as-received powders were dispersed in the dispersant and the ultrasonic for 5 min. After that sample was poured into small volume unit with stirrer to pass sample into the laser light. The scattered laser from the sample is detected by the receiver of the optical measurement unit. This data from the receiver is transmitted to the computer system where the operating software calculates the particle size and size distribution. It should be noted that a precise measurement up to the optical parameters. The refractive index and the absorption of the BNT-based powder was 2.45 and 0.0001, respectively.

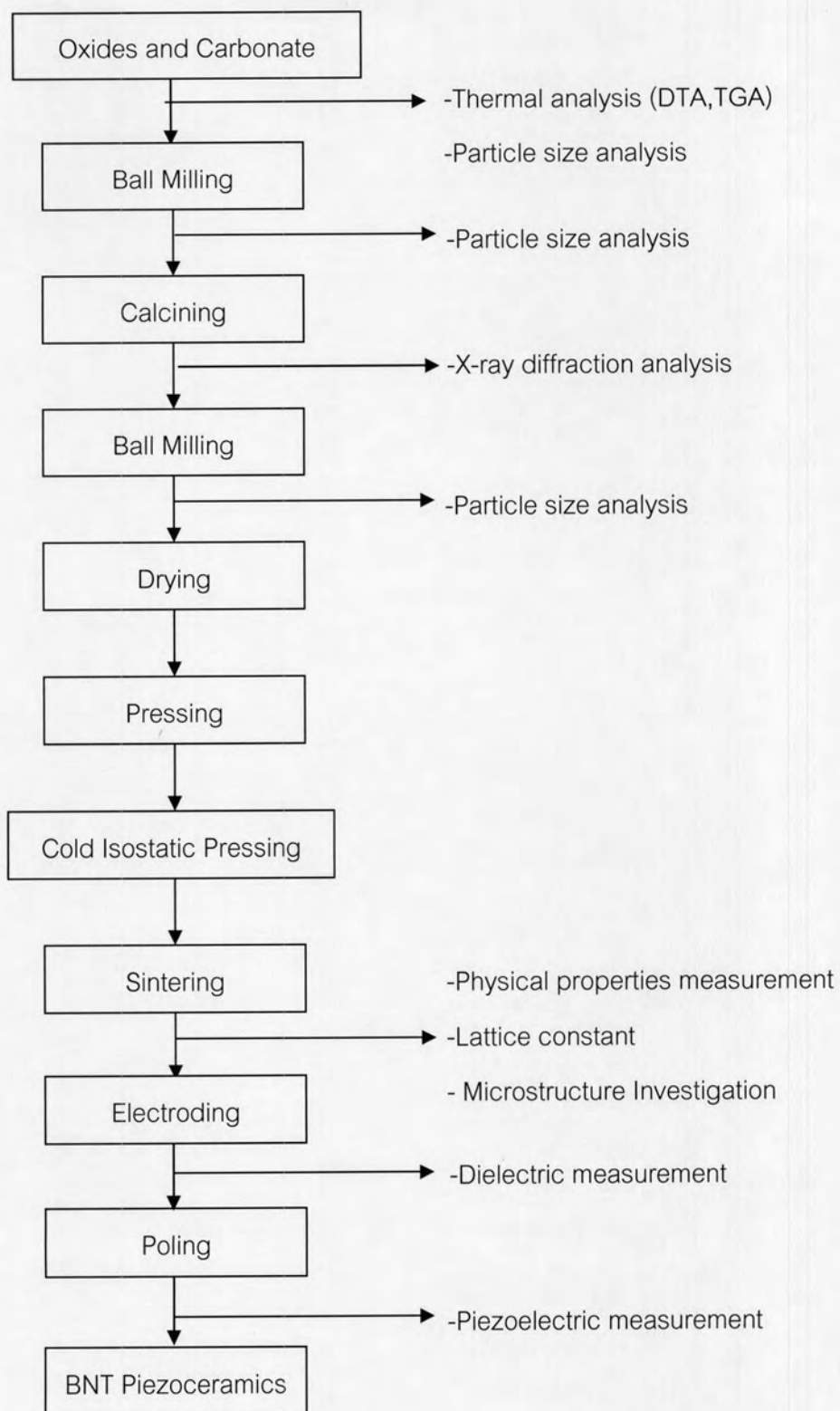


Fig. 3.2 A schematic flowchart of characterization and measurement methods

3.3.2 Thermal Analysis

Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were used to study the chemical and physical transformations during heating up of substances in the furnace. Thermogravimetric analysis (TG) is the study of the weight changes of a specimen as a function of temperature. This technique is useful strictly for transformations involving the absorption or evolution of gases from a specimen consisting of a condensed phase. The weight loss might be presents the releasing the surface water, molecular water or the decomposition of volatile matter at high temperature [37].

Differential thermal analysis (DTA) is the study of the transformations of the sample either absorb (endothermic) or release (exothermic) heat. The instrument will detect that the sample is cooler or hotter than the reference, and will indicate the transformation as endothermic and exothermic respectively on a plot of differential temperature versus time [37].

Differential scanning calorimeter (DSC) is similar to DTA technique. In the furnace, there are separate containers for both sample and reference which are heat at the same profile. As the sample temperature infinitesimally deviates from the reference temperature, the device detects it and reduces the heat input to one cell while adding heat to the other, so as to maintain a zero temperature difference between the sample and reference, establishing a null balance [37]. DSC is one of the other techniques to investigate the phase transitions of piezoelectric ceramics. The sintered sample should be ground into fine particles. Before testing, the sample powder must be taken in the oven at higher than 100°C to release the internal stress. In piezoelectric ceramics, the endothermic peak show the phase transition while heating up, and exothermic peak is shows the phase transition while cooling down.

3.3.3 X-ray Diffraction Analysis

The X-ray diffraction (XRD) method is widely used to qualitatively and quantitatively determine the phases present in sample. The measurement condition of XRD is shown in Table 3.7. The JCPDS file was used to identify the patterns of powders.

Table 3.7 Condition of X-ray diffraction analysis

Item	Condition
2θ	20-60 degree
step angle	0.02 degree
count time	1 second
X-ray source	1.54439 Å of CuK α
Voltage	30 kV
Current	40 mA

The lattice parameters were determined from the hkl reflections using a unit cell refinement program. Si standard (640C) was used as an internal standard to correct shift of d-spacing. To calculate lattice parameters of BNT compounds, the lattice parameters of a hexagonal structure were first measured and the results were transformed to a rhombohedral system as shown in the following equation [38]. Jade software (version 6.5) was used for the lattice parameter refinement.

$$a_R = \frac{1}{3} \sqrt{3(a_H)^2 + c^2} \quad (3.1)$$

$$\sin \frac{\alpha}{2} = \frac{3}{2 \sqrt{3 + \left(\frac{c}{a_H}\right)^2}} \quad (3.2)$$

Where a_H and c are lattice distances of the hexagonal structure, and a_R is lattice distance of the rhombohedral structure

The lattice parameters were used to calculate the volume and theoretical density of a unit cell by following equations.

$$V = a^3 \sqrt{1 - 3 \cos^2 \theta + 2 \cos^3 \theta} \quad (3.3)$$

$$D_{th} = \frac{MW \times 10^{24}}{V \times 6.02 \times 10^{23}} \quad (3.4)$$

Where V is lattice volume for a rhombohedral system,

a and θ are a lattice distance and angle respectively,

D_{th} is a theoretical density,

MW is a molecular weight of each composition.

3.3.4 Measurements of Other Physical Properties

A. Density Measurements

The densities of sintered specimens were measured according to ASTM C 373-88 [39]. The specimen were overnight dried at 100 °C then cooled down in desiccator and the dried mass, D , were determined. The specimens were placed in distilled water and boiled for 5 hrs taking care that the specimens are covered with water at all time, and then allow the specimens to soak for an additional 24 hrs. After impregnation of the specimens, the mass, S , of each specimen while suspended in water was determined. Each specimen was blotted lightly with a moistened, lint-free or cotton cloth to remove all exceeds water from the surface, and the saturated mass, M , was determined. The exterior volume, V (cm³), can be calculated as follows:

$$V = M - S \quad (3.5)$$

The volumes of open pores V_{op} (cm³), and impervious portions (closed pored and solid) V_{ip} (cm³), are given by:

$$V_{op} = M - D \quad (3.6)$$

$$V_{ip} = D - S \quad (3.7)$$

The apparent porosity, P (%), expresses as a percent, the relationships of the volume of the open pores of the specimen to its exterior volume. The apparent porosity can be calculated as follows:

$$P = \left(\frac{M - D}{V} \right) \times 100 \quad (3.8)$$

The water absorption, A (%), expresses as a percent, the relationship of the mass of water absorbed to the mass of the dry specimen. It can be determined as follows:

$$A = \left(\frac{M - D}{D} \right) \times 100 \quad (3.9)$$

The apparent density, T (g/cm^3), of that portion of the test specimen that is impervious to water, is given by:

$$T = \left(\frac{D}{D - S} \right) \quad (3.10)$$

The bulk density, B (g/cm^3), of a specimen is the quotient of its dry mass divided by the exterior volume, including pores, which can be calculated the bulk density as follows:

$$B = \left(\frac{D}{V} \right) \quad (3.11)$$

B. Volume Shrinkage Measurements

The volume shrinkage of the samples was determined according to ASTM C326 [40]. The volume of dried green samples, V_1 , were measured by calculate from the dimension of the samples, and then put the samples in the muffle furnace to sinter. After sintering step, the samples were then measured the fired volume, V_2 . The volume shrinkage is calculated by the following equation;

$$\%S_v = \left(\frac{V_1 - V_2}{V_1} \right) \times 100 \quad (3.12)$$

Where %S is the volume shrinkage (%),

V_1 is the dried volume of sample (cm^3),

V_2 is the fired volume of sample (cm^3).

3.4 Measurements of Dielectric, Electrical and Piezoelectric properties

3.4.1 Dielectric Properties Measurements

The capacitances and dissipation factor of all samples were measured at room temperature with various frequency of 1, 10, 100 kHz and 1 MHz using an impedance analyzer (L-C-R meter) model 4194A, Hewlett Packard, Inc. The dielectric constant was calculated from following equation.

$$K = \frac{C_p t}{A \epsilon_0} \quad (3.13)$$

Where K is the dielectric constant or relative permittivity of sample,

C_p is the sample capacitance (F),

ϵ_0 is the dielectric constant of free space (8.854×10^{-12} F/m),

A is sample electrode area (m^2),

T is the sample thickness (m).

Dissipation factor, $\tan \delta$, is the tangent of dielectric loss angle. $\tan \delta$ is determined by the ratio of effective conductance to effective susceptance in a parallel circuit, measured by an impedance analyzer (L-C-R meter) model 4194A, Hewlett Packard, Inc.

3.4.2 Volume Resistivity Measurements

The volume resistivity was measured at room temperature using an Resistivity Chamber (Keithley Model 6150). The equipment is composed with the resistivity chamber, the high voltage supply (Keithley 247) and the electrometer (Keithley 617). The samples were applied the electric field by the voltage supplier, then the electrometer was recorded the current value. The volume resistivity was calculated from following equation.

$$\rho = \frac{A \times V}{I \times t} \quad (3.14)$$

where ρ is the volume resistivity of sample (ohm-cm),

A is the area of sample (cm^2),

V is the applied voltage (volt),

t is the thickness of sample (cm),

I is the measured current (ampere).

3.4.3 Piezoelectric Properties Measurements

The piezoelectric charge coefficient, d_{33} of the sample was measured using a piezo d_{33} -meter. The d_{33} value is used to check the ability of poling process. The sample was put between two probes, which were applied mechanical pressed to the sample. The piezo meter convert the mechanical force into the electrical signal, and then d_{33} was displayed on the monitor.

The voltage piezoelectric coefficient, g_{33} were calculated by the following equation;

$$g_{33} = \frac{d_{33}}{K\epsilon_0} \quad (3.15)$$

Where K is the dielectric constant of the samples,

ϵ_0 is the dielectric constant of free space (8.853×10^{-12} F/m).

3.4.4 Other Piezoelectric Properties Measurements [10]

Electromechanical coupling factor, k is an indicator of an effectiveness with which a piezoelectric material converts electrical energy into mechanical energy. The dimension of ceramic can dictate unique expressions of k . For thin disc of piezoelectric ceramic the planar coupling factor, k_p , express radial coupling – the coupling between an electric field parallel to the direction in which the ceramic is polarized and mechanical effects that produce radial vibrations, relative to the direction of polarization. For a disc or plate of material which surface dimensions are large relative to its thickness, the thickness coupling factor, k_t , expresses the coupling between an electrical field in direction 3 and mechanical vibrations in the same direction. The k_p and k_t can calculate from following equations:

$$k_p = \sqrt{[(2.51(f_n - f_m)/f_n) - ((f_n - f_m)/f_n)^2]} \quad (3.16)$$

$$k_t = \sqrt{[(\pi/2)(f_n/f_m) \tan[(\pi/2)((f_n - f_m)/f_n)]]} \quad (3.17)$$

Where f_m is minimum impedance frequency (resonance frequency)(Hz)

f_n is maximum impedance frequency (anti-resonance frequency)(Hz)

Frequency constant, N , is the frequency of ceramic, when ceramic is exposed to a high frequency alternating electric field, with an impedance minimum and the planar or radial resonance frequency, coincides with the series resonance frequency, f_s . The relation

between the radial mode resonance frequency constant, N_p , and the diameter of ceramic, d , is expressed by:

$$N_p = f_s d \quad (3.18)$$

At the higher resonance, another impedance minimum, the axial resonance frequency, is encountered. The thickness mode frequency constant, N_t , is related to the thickness of ceramic, t , is expressed by:

$$N_s = f_s t \quad (3.19)$$