

## CHAPTER 3

### EXPERIMENTAL PROCEDURE

This chapter describes the experimental procedures and characterization techniques of the PMN-PZT ceramics. The procedure of the studies is shown as a flow diagram in figure 3.1. In this study, seven different PMN-PZT compositions were prepared using a solid-state mixed-oxide technique. Phase formation, microstructure and density of the sample were investigated using x-ray diffraction, scanning electron microscope (SEM) and Archimedes method, respectively. The ceramics were poled at different applied DC field strengths, and the hysteresis properties were measured by a conventional Sawyer-Tower circuit. The details of each experimental procedure will be described in the following sections.

#### **3.1. Sample preparation**

The main purposes of preparation methods are generally to create materials of desired composition, which meet specific properties for good electrical properties.

##### **3.1.1. Powder preparation**

PMN-PZT powders used in this study were prepared using a solid-state mixed oxide technique. Laboratory grade PbO (Fluka, 99.0% purity), ZrO<sub>2</sub> (Riedel-de Haën, 99.0% purity), TiO<sub>2</sub> (Riedel-de Haën, 99.0% purity), MgO (Fluka, 98.0% purity) and Nb<sub>2</sub>O<sub>5</sub> (Aldrich Chemical Company, Inc., 99.9% purity) were used as starting materials. The powder preparation procedure is shown in the diagram in figure 3.2. Stoichiometric mixtures of the appropriate starting materials were weighed. Mixing was performed by wet ball milling with zirconia balls and ethanol (Merck, 99.8% purity) as mixing agent in polyethylene jar for 24 hours. Drying was carried out on a hotplate with a magnetic stirring until the mixtures were dried. The dried mixtures were then ground before calcination. The dried mixtures were calcined in closed alumina crucible and then ground, sieved to give calcined powders.

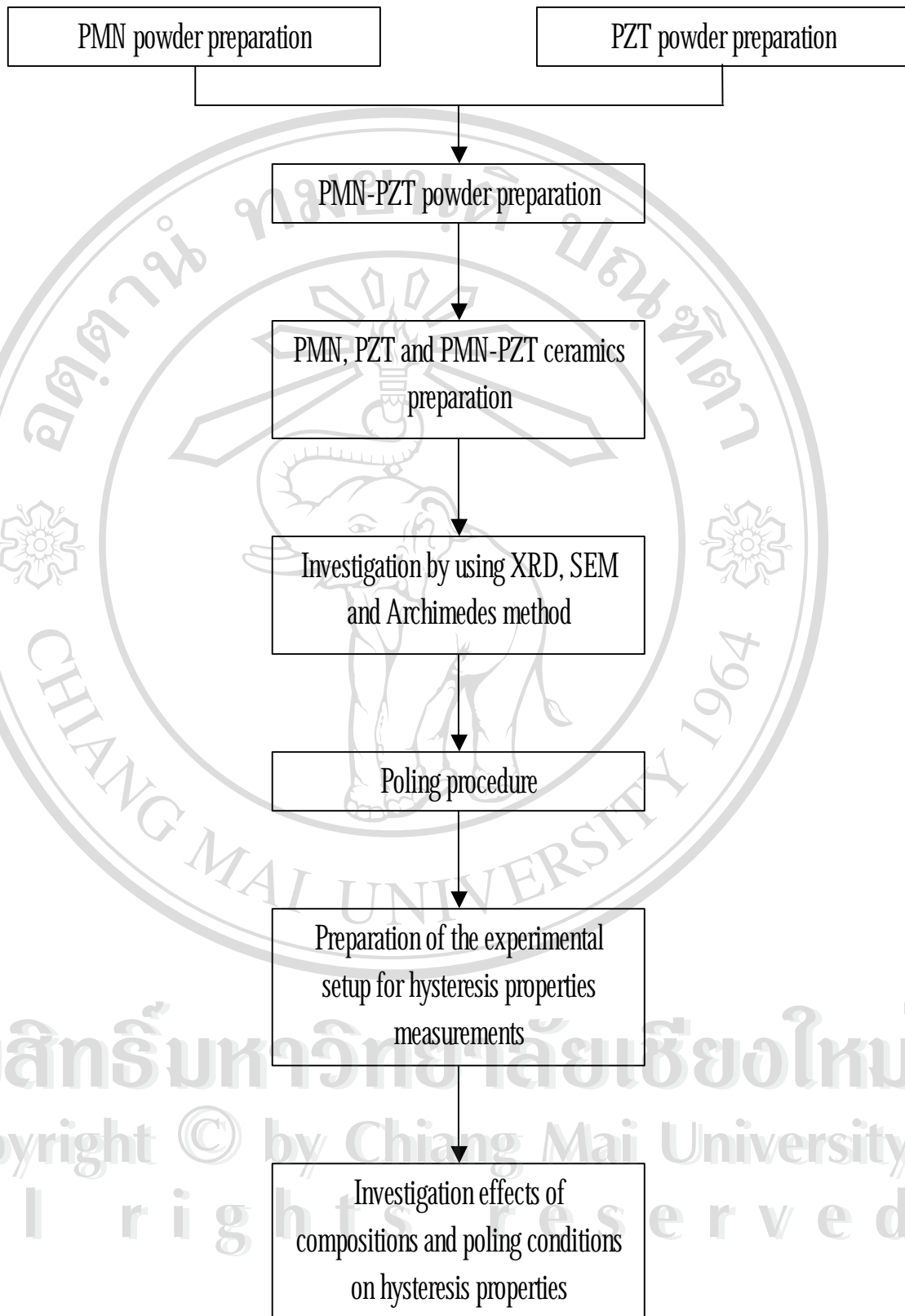


Figure 3.1 Experimental procedure diagram

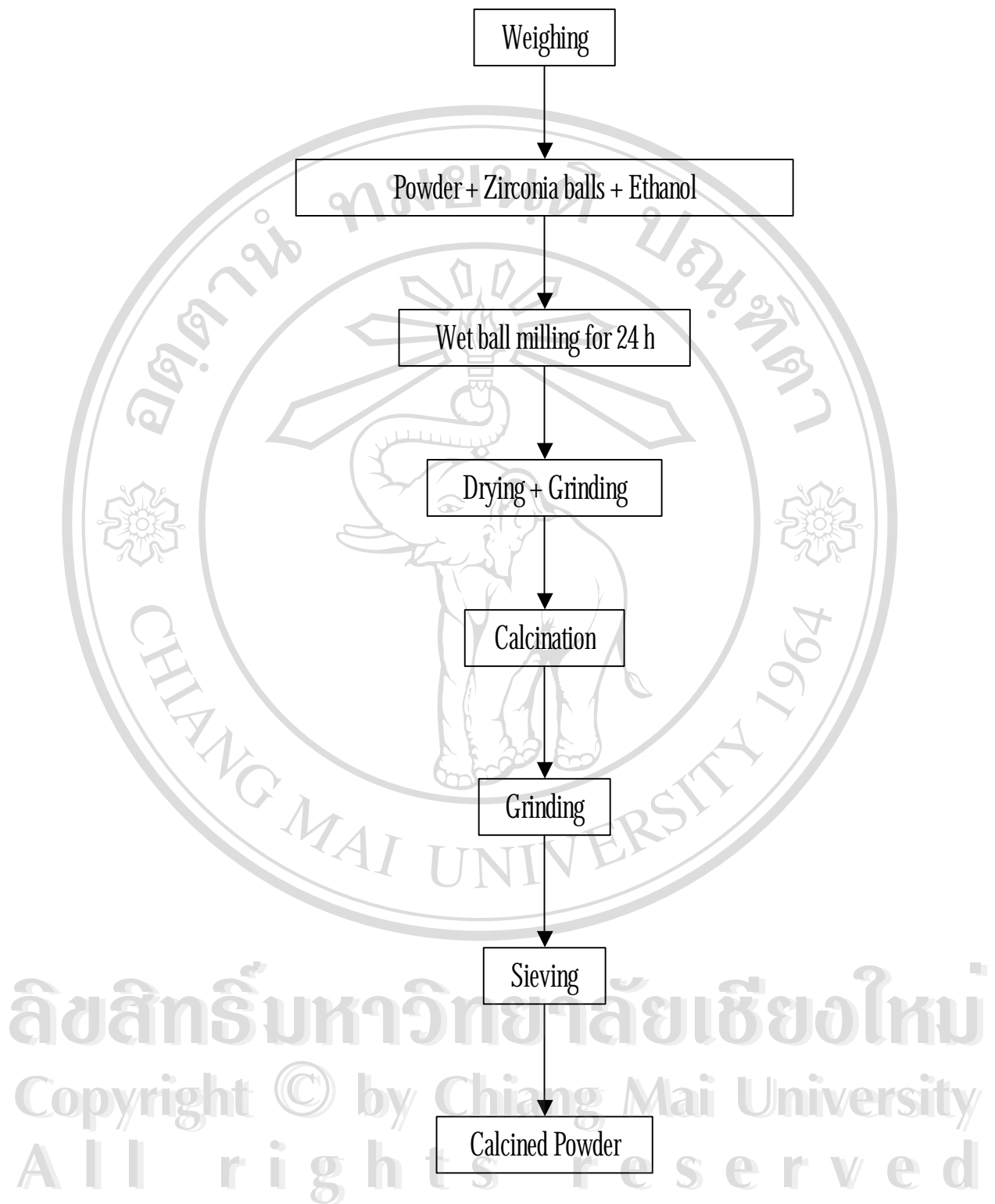


Figure 3.2 Preparation route for powder

### 31.1.1. Preparation of lead zirconate titanate powders

$\text{Pb}(\text{Zr,Ti})\text{O}_3$  powders was synthesized by the two-stage mixed-oxide, initially by the constituent oxides reacting to form a solid solution of zirconium titanate ( $\text{ZrTiO}_4$ ) and lead oxide ( $\text{PbO}$ ), which later to form the PZT phase.<sup>40</sup> The following reaction sequences are proposed for the formation of PZT:



The starting materials,  $\text{ZrO}_2$  and  $\text{TiO}_2$  were used for  $\text{ZrTiO}_4$  powder and the mixing process is described in figure 3.2. The  $\text{ZrTiO}_4$  was prereacted by calcining at  $1300\text{ }^\circ\text{C}$  for 4 hours with heating/cooling rates of  $20\text{ }^\circ\text{C}/\text{min}$ .<sup>41</sup>

The  $\text{ZrTiO}_4$  precursors were then mixed with  $\text{PbO}$  by powder processing as shown schematically in figure 3.2. The consequent mixed powders were calcined at  $950\text{ }^\circ\text{C}$  for 2 hours with  $20\text{ }^\circ\text{C}/\text{min}$  heating/cooling rates to give the final product of PZT powders.<sup>40</sup>

### 31.1.2. Preparation of lead magnesium niobate powders

To prevent pyrochlore formation, the B-site cations were prereacted using the columbite precursor method proposed by Swartz and Shrout.<sup>42</sup> The  $\text{MgNb}_2\text{O}_6$  precursors were first prepared from the reaction of  $\text{MgO}$  and  $\text{Nb}_2\text{O}_5$ .  $\text{PbO}$  was later reacted with  $\text{MgNb}_2\text{O}_6$  to give PMN as follows:



The  $\text{MgNb}_2\text{O}_6$  precursors were prepared by mixing process described in figure 3.2 with  $\text{MgO}$  and  $\text{Nb}_2\text{O}_5$  as starting powders. The mixing powders were calcined at  $1050\text{ }^\circ\text{C}$  for 2 hours with  $10\text{ }^\circ\text{C}/\text{min}$  heating/cooling rates.<sup>43</sup>

$\text{PbO}$  was then reacted with  $\text{MgNb}_2\text{O}_6$  precursors. The mixed powders were calcined at  $750\text{ }^\circ\text{C}$  for 4 hours with  $5\text{ }^\circ\text{C}/\text{min}$  heating/cooling rates to give PMN powders.<sup>43</sup>

### 31.1.3 Preparation of lead magnesium niobate - lead zirconate titanate powders

The prepared PMN and PZT powders were used as starting powders to form PMN-PZT powders. (x)PMN-(1-x)PZT compositions were formulated with the following values of x: 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0. PMN and PZT precursor powders were mixed in polyethylene jars with cylindrical  $ZrO_2$  grinding media and ethanol and milled for 24 hours. Then the mixed powders were dried on a hotplate with a magnetic stirring. The dried powders were then ground and sieved to give the PMN-PZT powders with different compositions.

### 31.2 Ceramics preparation

The PMN, PZT and PMN-PZT powders received from the processes described in previous sections were mixed with 3 wt% polyvinyl alcohol (PVA, Fluka) binder. The mixing powders were pressed by uniaxial hydraulic press at pressure of 1.5 tons to form the green pellets of 10 mm diameter. The green pellets were placed on the lead zirconate powder - bed inside an alumina crucible. To minimize the lead loss, a PbO rich atmosphere was maintained with an equimolar mixture of PbO- $ZrO_2$ .

Sintering of the green pellets was performed by the sintering process described in figure 3.3 with a binder burn-out process at 500 °C for 2 hours. For optimization purpose, the (x)PMN-(1-x)PZT ceramics were sintered at different conditions as shown in Table 3.1.

For the electrical properties measurement, the sintered pellets were lapped to obtain parallel faces, and the faces were then coated with silver paint as electrodes. The samples were heat-treated at 750 °C for 12 minutes with 5°C/min heating/cooling rates to ensure good electrode conduction.

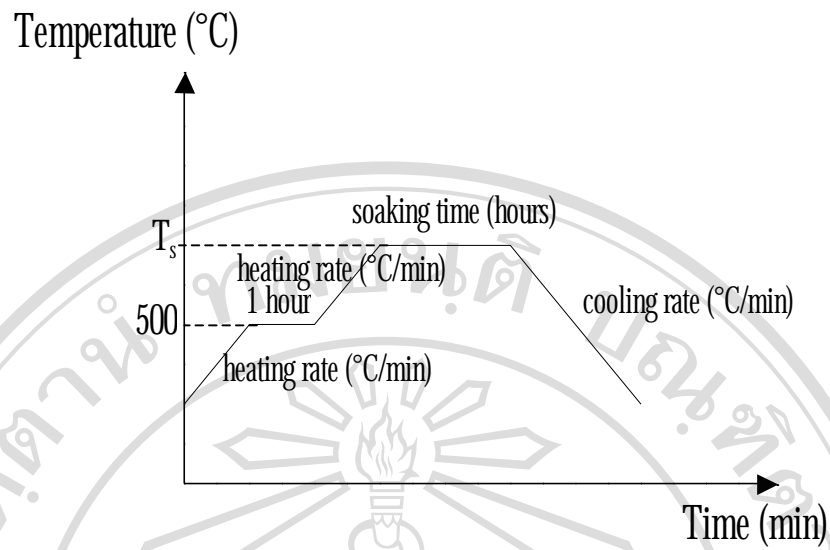


Figure 3.3 Sintering process diagram  
(when  $T_s$  is sintering temperature)

Table 3.1 Sintering temperature, dwell time, and heating/cooling rates for (x)PMN-(1-x)PZT ceramics.<sup>42</sup>

Ceramics	Sintering temperature (°C)	Dwell time (hours)	Heating/cooling rate (°C/min)
PMN	1225	4	5
0.1PMN-0.9PZT	1275	4	20
0.3PMN-0.7PZT	1275	6	1
0.5PMN-0.5PZT	1275	6	5
0.7PMN-0.3PZT	1275	4	10
0.9PMN-0.1PZT	1250	4	5
PZT	1250	4	10

### 31.3 Poling procedure

For the electrical properties especially hysteresis properties measurements, (x)PMN-(1-x)PZT samples need to be poled to re-orient the direction of the spontaneous polarization. To pole a ceramic, the sample was placed in the sample holder in a silicone oil bath. The poling setup is shown in figure 3.4. To study the effects of poling conditions, the samples were poled in heat-bath at a temperature of 110°C by applying a DC electric field (from high voltage source) in the range of 10-40 kV/cm for 30 minutes and then field-cooled to room temperature.<sup>8</sup> The poled samples were left for 24 hours before measurements.

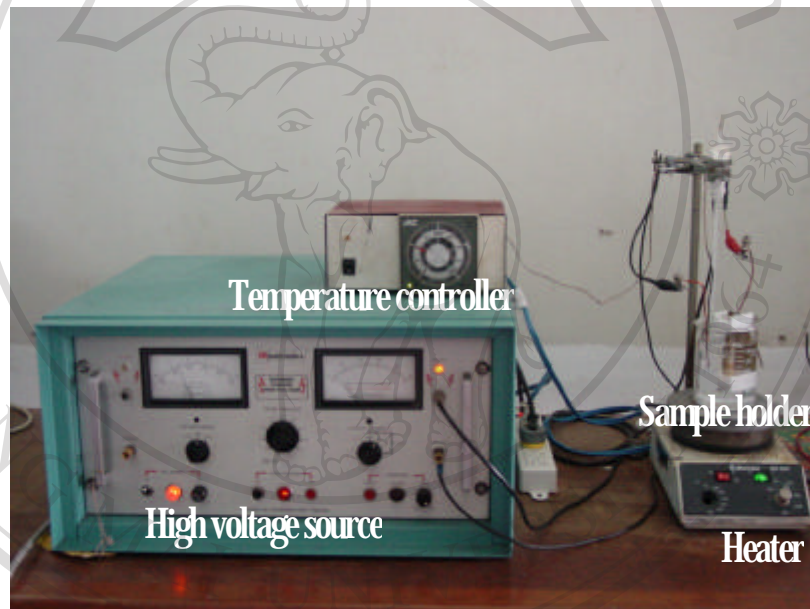


Figure 3.4 Poling setup used to pole samples in this study

### 3.2 Sample characterizations

Characterization techniques used for subsequent investigation of phase formation, microstructural and specimen density were x-ray diffraction, scanning electron microscope (SEM) analyses of fracture surfaces and Archimedes density, respectively.

### 3.2.1. The X-ray diffraction (XRD) technique

XRD patterns were used to analyze phase formation behavior and phase purity, which was especially important in minimizing pyrochlore phase formation in PMN-based compounds of the powders after calcination and sintering processes. The patterns were recorded between  $\theta = 20^\circ$  and  $60^\circ$ . A SIEMEN-D500 diffractometer with  $\text{CuK}_{\alpha}$  radiation at 40 kV, shown in figure 3.5, was used to obtain the patterns.

The relative amount of perovskite and pyrochlore phases were estimated from the major peak intensities of the perovskite and pyrochlore peaks using the following equation:

$$\% \text{ Pyrochlore} = \frac{I_{\text{pyro.}}}{I_{\text{perov.}} + I_{\text{pyro.}}} \times 100 \quad (3.5)$$

where,  $I$  represents the intensity of phases.



Figure 3.5 X-ray diffractometer used in this study



### 3.2.2 Scanning electron microscopy (SEM)

Microstructural characterization of sample fracture surfaces using scanning electron microscopy (SEM) was used to determine the grain size and the presence of porosity. Average grain size of the sintered ceramics were estimated by using a linear intercept method<sup>44</sup>, where random lines were drawn on a micrograph and the number of grain boundaries intercepting these lines were then counted. JEOL JSM-840A scanning electron microscope was used for this study, as shown in figure 3.6.

### 3.2.3 Densification analysis

The weight loss due to PbO volatility after sintering was investigated by densification analysis. The densities were determined by a method based on the Archimedes principle.

The samples were boiled for 1 hour and left to cool to room temperature before recording the weights of the samples in water ( $w_3$ ) and the wet sample in air ( $w_2$ ). Weights of dried samples in air ( $w_1$ ) were also recorded. Density of each sample was calculated by following equation:

$$r_c = \frac{w_1}{w_2 - w_3} \approx \frac{w_1}{w_2 - w_3} r_{H_2O} \quad (3.6)$$

Where,  $r_{H_2O}$  is the density of water at room temperature.

$r_c$  is the density of sample at room temperature.

$w_1$  is the weight of the dried sample in air.

$w_2$  is the weight of the wet sample in air.

$w_3$  is the weight of the sample in water.



Figure 3.6 Scanning electron microscopy (SEM) used in this study

### 3.3 Experiment setup for hysteresis properties measurement

To measurement hysteresis properties, a standard Sawyer-Tower circuit<sup>12</sup>, as shown in figure 3.7, was employed. The experiment setup was designed to measure the sample's response under an external electric field (figure 3.8). Sinusoidal signals generated by a signal generator (model GAG-809, Good well instrument, CO.LTD) were amplified (model 610D, TREK, INC.) and applied to the sample and to a standard capacitor in series. The voltage ( $V_y$ ) developed on the standard capacitor, due to the polarization of the sample, was fed to the Y-axis (or  $V_y$ ) of an X-Y oscilloscope (model HM 303-6, HAMEG Instruments) as shown in figure 3.9. The electric field, measured on the X-axis (or  $V_x$ ), was also fed to the oscilloscope through an attenuation resistor by a potential divider principle. All the measurements were carried out at frequency of 50 Hz. An experimental setup was calibrated through measurement of hysteresis loops of commercial PZT samples (PKI-552, Piezo Kinetics Incorporated (Pennsylvania, USA)). Figure 3.9 shows an example of hysteresis loop obtained from the set-up.

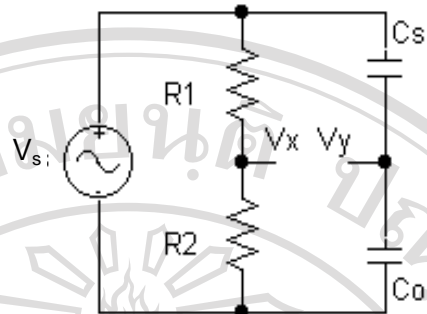


Figure 3.7 Schematic of the standard Sawyer-Tower circuit  
 ( $R_1 = 6.8 \text{ M}\Omega$ ,  $R_2 = 10 \text{ k}\Omega$ ,  $C_0 = 0.1 \mu\text{F}$ ,  $C_s = \text{Sample}$ ,  $C_0 \gg C_s$ )

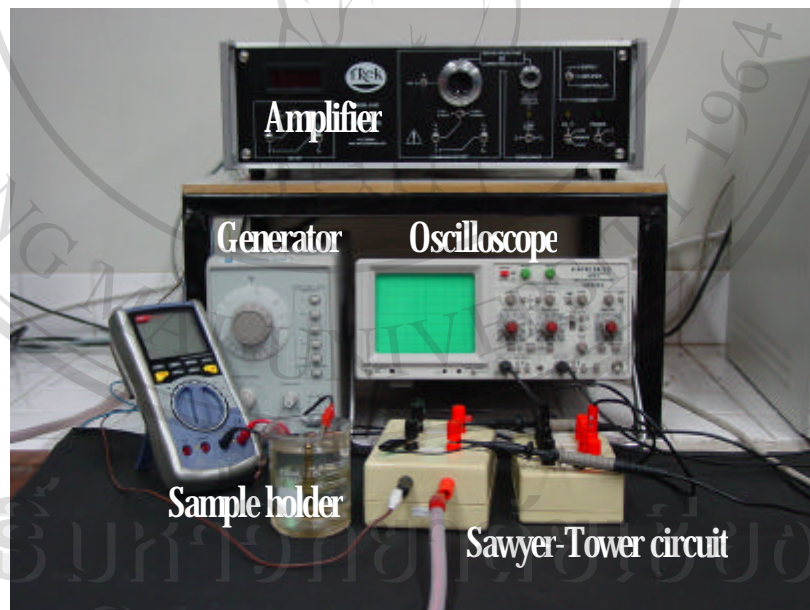


Figure 3.8 The experiment setup for hysteresis loop measurements

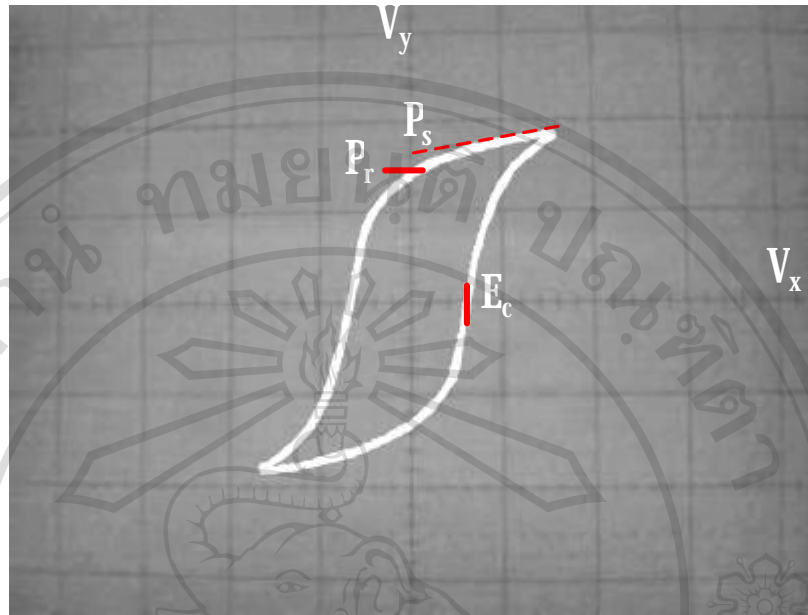


Figure 3.9 Example of a hysteresis loop obtained from the experimental set-up

From each measurement, the poled ceramic was placed in the sample holder, which was submerged in a silicone oil to prevent on electric breakdown. The sample was then connected to the standard capacitor on Sawyer-Tower circuit. The sample could be considered as a capacitor ( $C_s$ ) connected in series to the standard capacitor ( $C_o$ ). Since the capacitance of the sample was much smaller than that of the standard capacitor, almost all of the electric potential of the high voltage source acts on the samples.

By definition, polarization is the value of dipole moment per unit volume or amount of charge accumulated per unit surface area. Polarization of the sample induced by electric field loading,  $P_{sample}$  was given by

$$P_{sample} = \frac{Q_s}{A} \quad (3.7)$$

Where,  $Q_s$  is the amount of charges accumulated on the electrode of the sample

$A$  is the area of the electrode of the sample

Since the reference capacitor was connected in series to the sample, then amount of charges are equivalent:

$$Q_s = Q_0 \quad (3.8)$$

Where,  $Q_0$  is the amount of charges accumulated on the standard capacitor.

On the other hand, the amount of charges on the standard capacitor is equal to

$$Q_0 = V_y C_0 \quad (3.9)$$

Where,  $V_y$  is the voltage across the standard capacitor, and  $C_0 = 0.1 \mu F$ , is the capacitance of the standard capacitor.

Then the polarization induced by electric field loading could be calculated as

$$P_{sample} = \frac{V_y C_0}{A} \quad (3.10)$$

Consequently, by monitoring the voltage across the standard capacitor, the polarization of the sample could be determined.

From the X-axis of the monitor of oscilloscope, the electric field was calculated using the following equation:

$$E = \frac{V_x}{d} \quad (3.11)$$

Where,  $V_x$  is the voltage across the sample

$d$  is the thickness of the sample

The voltage across the sample was derived from potential divider principle where  $R_1$  was connected to  $R_2$  in series.

### 3.4 Measurements of hysteresis properties of lead magnesium niobate - lead zirconate titanate ceramics

The P-E behaviors of PMN-PZT ceramics were measured by a Sawyer-Tower Circuit. The measurement set-up is described in previous section. Since the objective of this study is to investigate the effects of poling conditions and the composition ratio on the hysteresis properties of PMN-PZT ceramics, therefore many compositions of PMN-PZT ceramics poled at various poling field strengths were used. The measurement steps are described as follows:

1. Sample was clamped with a holder in silicone oil bath.
2. The voltage was applied to the sample from zero voltage until the maximum voltage, where the P-E loop reaches saturation.
3. The developed hysteresis loop was recorded step by step from zero voltage until the maximum voltage.
4. Calculation of spontaneous polarization, remanent polarization and coercive field was carried out using and the equation described in previous section. From the hysteresis loop shown in figure 3.9 many hysteresis parameters can be obtained. The value of polarization at zero fields is called the remanent polarization ( $P_r$ ), which is determined from the intercept of hysteresis loop with the Y-axis. Of interest also is the spontaneous polarization ( $P_s$ ) obtained by extrapolating the polarization at high field  $P_s$  back to zero field along a tangent (Y-axis).  $P_s$  itself is a function of the peak field.  $P_s$  is somewhat higher than  $P_r$  in ceramic, but is virtually equal to  $P_r$  in crystals. The field necessary to bring the polarization to zero is called the coercive field ( $E_c$ ), which is determined from the intercept of hysteresis loop with the X-axis.
5. The information obtained is subsequently used to investigate the dependence of the hysteresis properties on the poling conditions and the composition ratio of PMN-PZT ceramics.