CHAPTER 3

EXPERIMENTAL PROCEDURES

This chapter contains the description of the basic methodology for ferroelectric dynamic hysteresis properties measurement and experimental setups for ferroelectric hysteresis investigation in $BaTiO_3$ [BT] single crystals, $BaTiO_3$ [BT] bulk ceramics, $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ [0.7PMN–0.3PT] single crystals and $(1\text{-}x)Pb(Zr_{1/2}Ti_{1/2})O_3\text{-}(x)Pb(Zn_{1/3}Nb_{2/3})O_3$ [(1-x)PZT-(x)PZN] ceramic systems (where x = 0.1, 0.2, 0.3, 0.4, and 0.5). The details are presented in the following sections.

To support the hypothesis that materials with similar domain states should have very comparable dynamic hysteresis and scaling behavior; in the first section, BT single crystal is chosen to determine dynamic hysteresis responses and its scaling relations at room temperature compared to previous investigations, such as in soft and hard PZT ceramics [16-17]. Simultaneously, polycrystalline BT ceramic is observed to clarify the influence of domain homogeneity on dynamic hysteresis and scaling behaviors compared to BT single crystal. The 0.7PMN-0.3PT single crystal, a relaxor ferroelectric material, is also observed scaling manners compared to normal ferroelectric BT single crystal. Finally, PZT-PZN ceramic systems with various compositions providing various crystal structures are investigated for the dependence of hysteresis behaviors and scaling conducts on domain structure.

In the second section, the dynamic hysteresis and scaling behaviors in BT single crystal and BT bulk ceramic are observed to confirm contribution of domain structure in controlling hysteresis properties. And in the final section, the electric field–waveform dependence of hysteresis behaviors and scaling relations in 0.7PMN-0.3PT single crystal is determined to clarify the influence of different field-waveform applications.

All specimens used in all these investigations were dedicated by many colleagues who were studying such materials. The details on fabrication and characterization of BT single crystal can be found in [119-122], BT bulk ceramic in Tangsritragul *et al.* [123], 0.7PMN-0.3PT single crystal in IBULE PHOTONICS, Inc. [124], and PZT-PZN ceramic systems in Triamnak *et al.* [125].

3.1 Basic methodology for dynamic hysteresis properties measurement

The ferroelectric hysteresis (*P*-*E*) loops of interested specimens are characterized by using a modified Sawyer-Tower circuit, as shown in Figure 3.1.

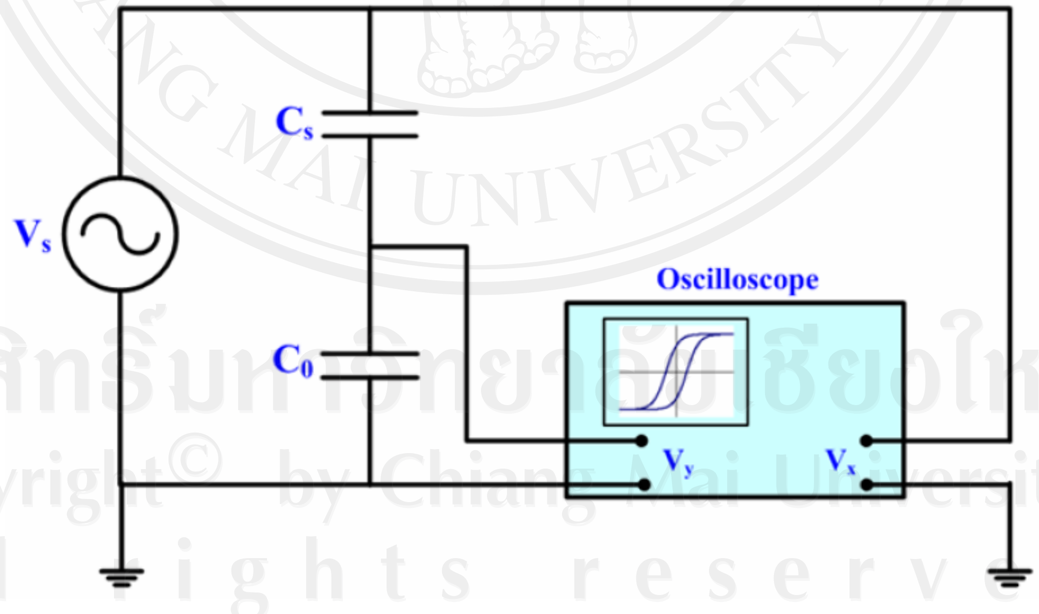


Figure 3.1 Schematic of the modified Sawyer-Tower circuit (C_0 = standard capacitor, C_s = Specimen, $C_0 >> C_s$)

The modified Sawyer-Tower circuit is designed to measure the specimen's response under applied frequency f and electric field E_0. Electric field signals generated by a signal generator are amplified and applied to specimen and to a standard capacitor in series. The voltage (V_y) developed on the standard capacitor, due to the polarization of the specimen, is fed to the Y-axis (or V_y) of an X-Y scope on computer. The electric field, measured on the X-axis (or V_x), is also fed to X-Y scope, combining as *P-E* hysteresis loop as shown in Figure 3.2. The measurements are carried out on discrete frequency and electric field. Figure 3.2 shows an example of hysteresis loop obtained from the setup.

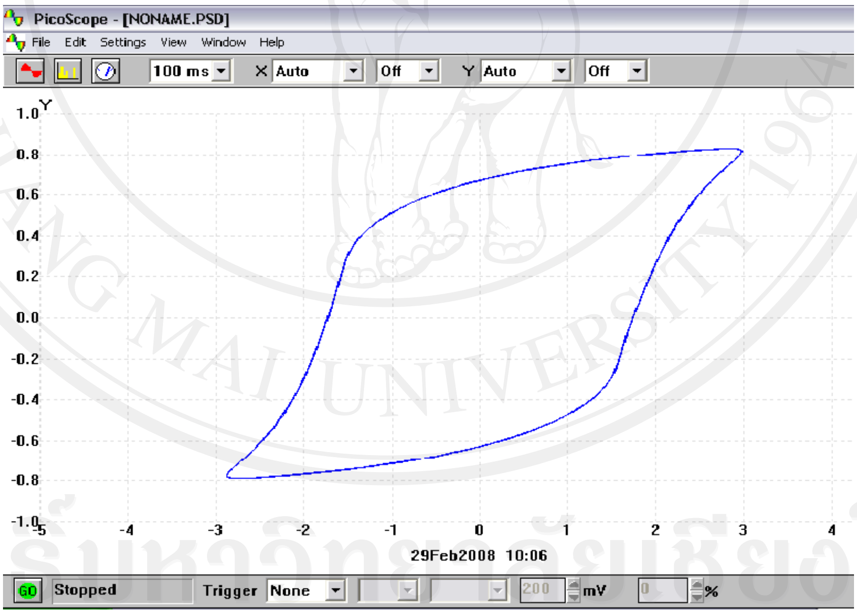


Figure 3.2 The P-E hysteresis loop of ferroelectric specimen on picoscope program

During measurements, the specimen is connected to the standard capacitor on modified Sawyer-Tower circuit. The specimen could be considered as a capacitor (C_s) connected in series to the standard capacitor (C_0). Since the capacitance of the specimen is much smaller than that of the standard capacitor, almost all of the electric potential of the high voltage source acts on the specimen.

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

$$P_{specimen} = \frac{Q_s}{A} \tag{3.1}$$

where, $P_{specimen}$ is polarization of specimen (unit, C/cm^2).

Q_s is the amount of charges accumulated on the electrode of the specimen (unit, C).

A is the area of the electrode of the specimen (unit, cm^2).

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

$$Q_s = Q_0 \tag{3.2}$$

where, Q_0 is the amount of charges accumulated on the standard capacitor (unit, C).

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

$$Q_0 = V_y C_0 \tag{3.3}$$

where, V_y is the voltage across the standard capacitor (unit, V), and C_0 is the capacitance of the standard capacitor (unit F).

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

$$P_{specimen} = \frac{V_y C_0}{A} \quad (3.4)$$

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

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

$$E = \frac{V_x}{d} \quad (3.5)$$

where, E is electric field applied to specimen (unit, V/cm).

V_x is the voltage across the circuit (unit, V).

d is the thickness of the specimen (unit, cm).

3.2 Experimental setups for hysteresis properties measurement

3.2.1 The procedures for the dynamic hysteresis investigation at room temperature

The interested specimen is carefully placed between the two alumina blocks in cylindrical brass cell and the electric field is applied to the specimen via the copper shims attached to the alumina blocks, as shown in Figure 3.3. During the measurements, the specimen is immersed in silicone oil to prevent high-voltage arcing during electrical loading.

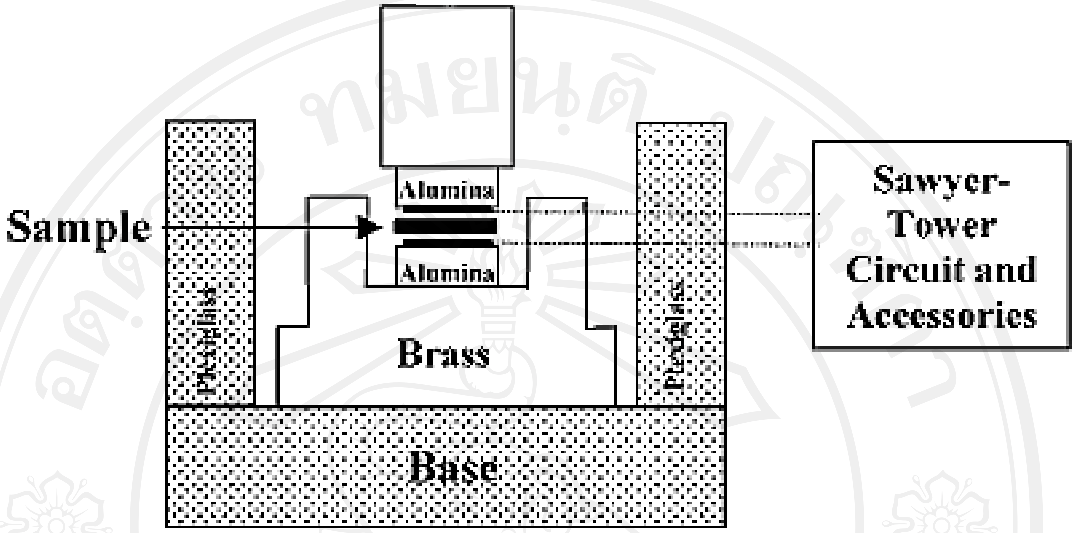


Figure 3.3 Schematic of the experimental set-up for dynamic hysteresis investigation at room temperature.

Measurements are performed as a function of frequency f and electric field E_0. During the measurements, a desired electric field is first applied to the specimen and then desired frequency is applied by a high voltage ac amplifier (Trek 610D) with the input sinusoidal signal from a function generator (HP 3310A). The developed ferroelectric hysteresis (P-E) loop is recorded by a digital oscilloscope (HP 54645A, 100 MHz) on discrete frequency and electric field. The parameters obtained from the loops are saturated polarization (P_{sat}), remnant polarization (P_r) and coercive field (E_C), which are defined as the point where the loops reach the maximum polarization, cross the zero field and cross the zero polarization, respectively. The ferroelectric parameters are obtained after a total of 20 cycles of the electric field application to average out the noise deformation. The setup is shown in Figure 3.4.

Figure 3.4 The setup for ferroelectric hysteresis loop measurement

The *P-E* behaviors of concerned specimen are measured by a modified Sawyer-Tower Circuit described in previous section. The objective of the study is to investigate the dynamic hysteresis behaviors under influence of frequency and electric field in ferroelectric materials. The measurement steps at room temperature are described as follows:

1. Specimen is placed between the two alumina blocks attached copper shims and immersed in silicone oil brass.
2. The desired field amplitude is applied to the specimen along frequency in range of interest.
3. At constant desired field amplitude, frequencies are varied as discrete value and then the developed hysteresis (*P-E*) loops are recorded by picoscope program interfaced on computer.

4. When all (*P-E*) hysteresis loops obtained from varying discrete frequency over interested range at constant field amplitude are completely recorded, then applied field amplitudes are varied as discrete value within range of interest which each fixed discrete field amplitude, frequencies are varied following previous steps. Polarization hysteresis loops are recorded in all variations.
5. All steps above are used for all investigated specimens.
6. The information obtained subsequently is used to investigate the dependence of the dynamic hysteresis properties on the domain structure of ferroelectric materials.

<u>Denote</u>; Range of frequency and field amplitude depends on investigated specimens.

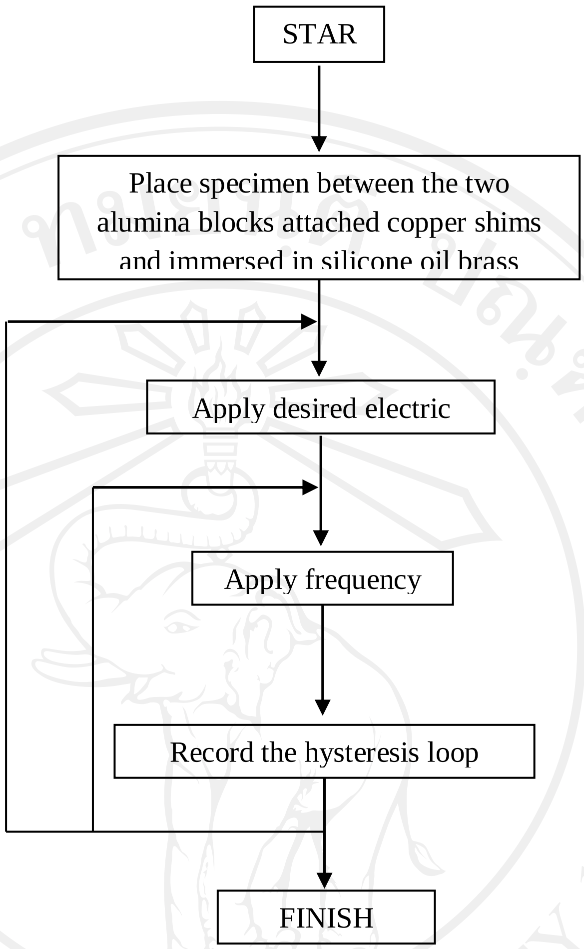


Figure 3.5 Flow chart of the dynamic hysteresis measurement at room temperature

3.2.1.1 Investigation in BT system

BT single crystals

The dynamic hysteresis (*P*-*E*) loops of tetragonal {001}-$BaTiO_3$ single crystal grown by the Remeika process [119-120] containing *a*-*c* domains [121-122] (triangular-shaped plates with 5 mm edge length and thickness of 0.5 mm) coated with silver paste at the top and bottom surface as an electrode are characterized at room temperature (25 °C) by using a modified Sawyer-Tower circuit with f covering from 1 to 300 Hz and E_0 from 0 to 6.6 kV/cm. Measurements are parallel to the tetragonal (001) direction [24].

Figure 3.6 BT single crystal specimens

BT bulk ceramics

The dynamic hysteresis (*P*-*E*) loops of tetragonal $BaTiO_3$ bulk ceramic prepared by a conventional mixed-oxide method, T_C = 124.5 °C, ε_r at 100 kHz = 1143, tan δ at 100 kHz = 0.0477, with a diameter of 8 mm and thickness of 1 mm coated with silver paste at the top and bottom surfaces as an electrode are characterized at room temperature (25 °C) by using a modified Sawyer-Tower circuit with f covering from 1 to 100 Hz and E_0 from 0 to 15 kV/cm [126].

Figure 3.7 BT bulk ceramic specimens

3.2.1.2 Investigation in 0.7PMN-0.3PT single crystals

0.7PMN-0.3PT single crystals

Commercial $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ [0.7PMN–0.3PT] single crystal (IBULE PHOTONICS, Inc.) of square shape 5 x 5 mm^2 and thickness 0.65 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated at room temperature (25 °C). The polarization-electric field (*P-E*) hysteresis loops are conducted by using a modified Sawyer–Tower circuit in conjunction with computer controller. The system is capable of precise measurement of *P-E* behavior over the frequency range of 1 to 200 Hz. The electric field is applied from 0 to 15 kV/cm.

Figure 3.8 0.7PMN-0.3PT single crystal specimens

3.2.1.3 Investigation in (1-x)PZT-(x)PZN ceramic systems

(1-x)PZT-(x)PZN; x = 0.1

The disc-shaped specimen of tetragonal-structure 0.9PZT-0.1PZN ceramic with diameter of 10 mm and thickness of 1 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated. The dynamic hysteresis (*P*-*E*) loops were characterized at room temperature (25 °C) by using a modified Sawyer–Tower circuit with *f* covering from 2 to 100 Hz and E_0 from 0 to 18 kV/cm [127].

(1-x)PZT-(x)PZN; x = 0.2

The disc-shaped specimen of mixing tetragonal and rhombohedral-structure 0.8PZT–0.2PZN ceramic with diameter of 10 mm and thickness of 1 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated. Its basic properties are dielectric constant (1 kHz) ε_r = 1575; Curie temperature T_C = 340 °C; piezoelectric strain constants d_{33} = 430 pm/V; planar coupling factor k_p = 0.58;

mechanical quality factor Q_m = 90; coercive field (10 Hz) E_C = 19.7 kV/cm. The dynamic hysteresis (*P*–*E*) loops are characterized at room temperature (25 °C) by using a modified Sawyer–Tower circuit with *f* covering from 2 to 100 Hz and E_0 from 0 to 16 kV/cm [128].

(1-x)PZT-(x)PZN; x = 0.3

The disc-shaped specimen of rhombohedral-structure 0.7PZT–0.3PZN ceramic with a diameter of 10 mm and a thickness of 1 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated. Its basic properties are dielectric constant (1 kHz) ε_r = 1625; Curie temperature T_C = 313 °C; piezoelectric strain constant d_{33} = 443 pm/V; planar coupling factor k_p = 0.57; mechanical quality factor Q_m = 66; coercive field (10 Hz) E_C = 13.1 kV/cm. The dynamic hysteresis (*P*–*E)* loops are characterized at room temperature (25 °C) by using a modified Sawyer–Tower circuit with *f* covering from 2 to 100 Hz and E_0 from 0 to 12 kV/cm [129].

(1-x)PZT-(x)PZN; x = 0.4

The disc-shaped specimen of rhombohedral-structure 0.6PZT–0.4PZN ceramic with a diameter of 10 mm and thickness of 1 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated. Its basic properties are dielectric constant (1 kHz) ε_r = 1616; Curie temperature T_C = 284 °C; piezoelectric strain constants d_{33} = 457 pm/V; planar coupling factor k_p = 0.59; mechanical quality factor Q_m = 62; coercive field (10 Hz) E_C = 12 kV/cm. The dynamic hysteresis (*P*–*E*) loops are characterized at room temperature (25 °C) by a modified Sawyer–Tower circuit with *f* ranging from 2 to 100 Hz and E_0 from 0 to 10.5 kV/cm [130].

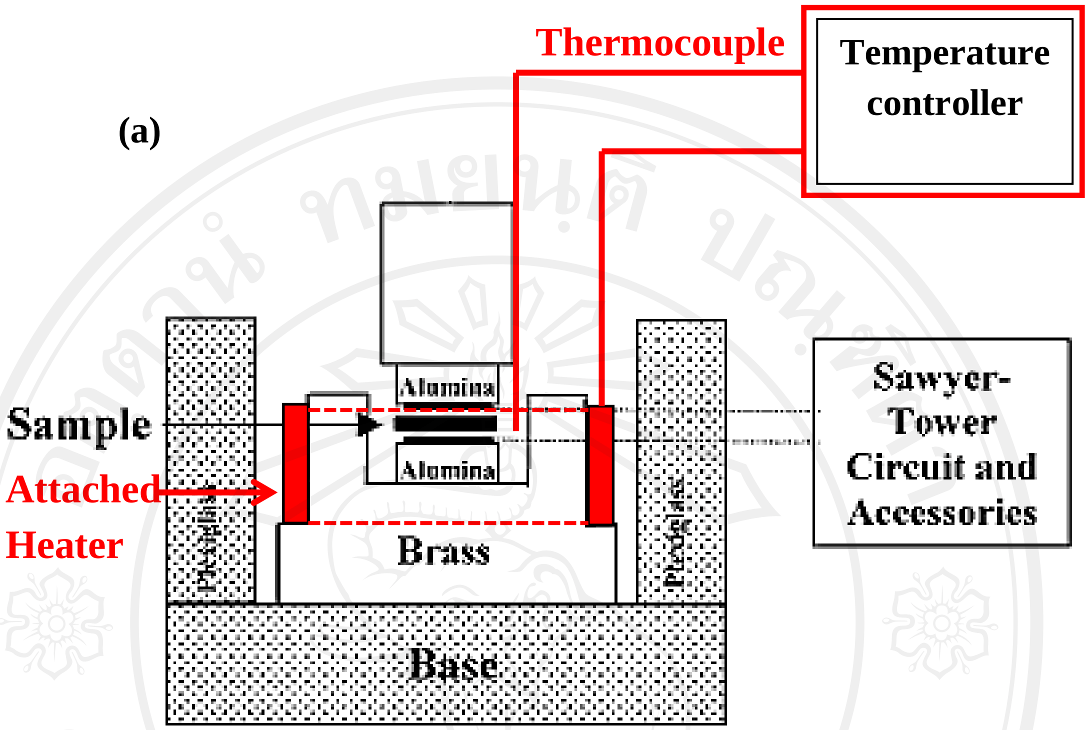
(1-x)PZT-(x)PZN; x = 0.5

The disc-shaped specimen of rhombohedral-structure 0.5PZT–0.5PZN ceramic with diameter of 10 mm and thickness of 1 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated. Its basic properties are dielectric constant (1 kHz) ε_r = 1566, Curie temperature T_C = 256 °C; piezoelectric strain constants d_{33} = 497 pm/V, planar coupling factor k_p = 0.60, mechanical quality factor Q_m = 54, and coercive field (10 Hz) E_C = 10 kV/cm. The dynamic hysteresis (*P-E*) loops are characterized at room temperature (25 °C) by using a modified Sawyer–Tower circuit with *f* covering from 2 to 100 Hz and E_0 from 0 to 9.6 kV/cm [19].

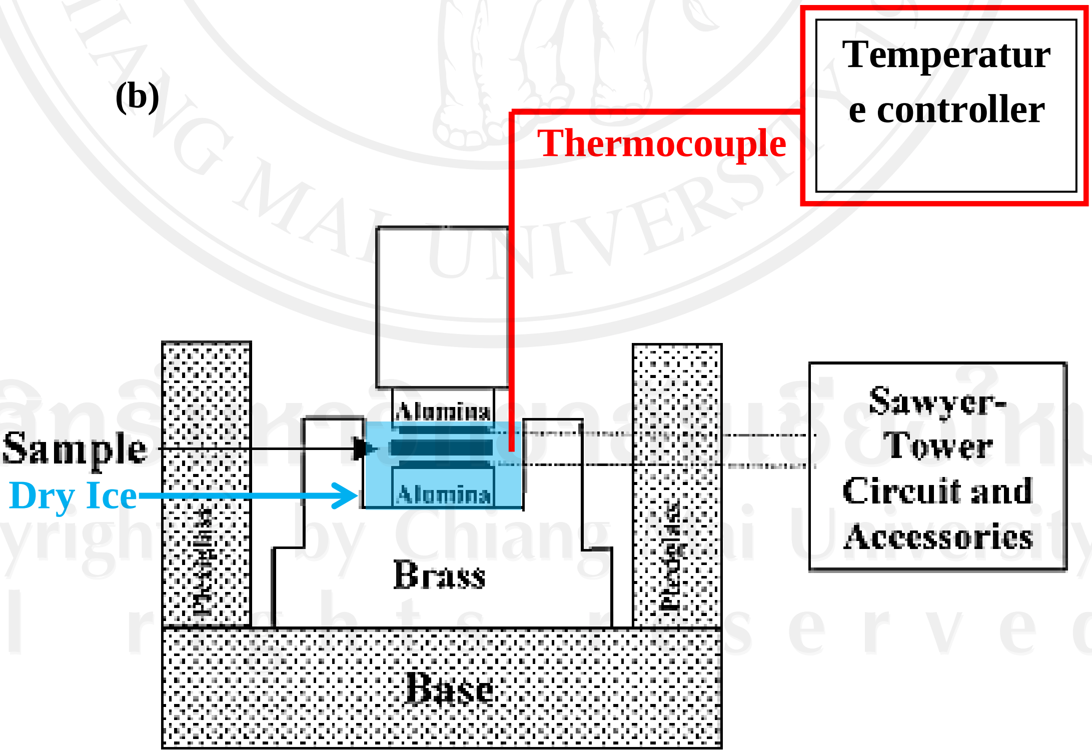
3.2.2 The procedures for the dynamic hysteresis investigation with temperature

To study the effects of temperature on the ferroelectric properties, the modified heating-hysteresis measurement setup is constructed. The setup is developed for simultaneous applications of the electrical loading and heat. It consists of a cylindrical brass cell attached with 300 watts of heater on a heavy brass base. Heat is applied by heater attached to brass cell (76 mm X 45 mm, 300 watts, 220 V), then applied heat is monitored and controlled by the temperature controller (JCS-33A-R/M.BK), as seen in Figure 3.9(a).

(a)


Thermocouple
Temperature controller
Alumina
Sample
Alumina
Attached Heater
Brass
Base
Sawyer-Tower Circuit and Accessories

(b)


Temperature controller
Thermocouple
Alumina
Sample
Dry Ice
Alumina
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(c)

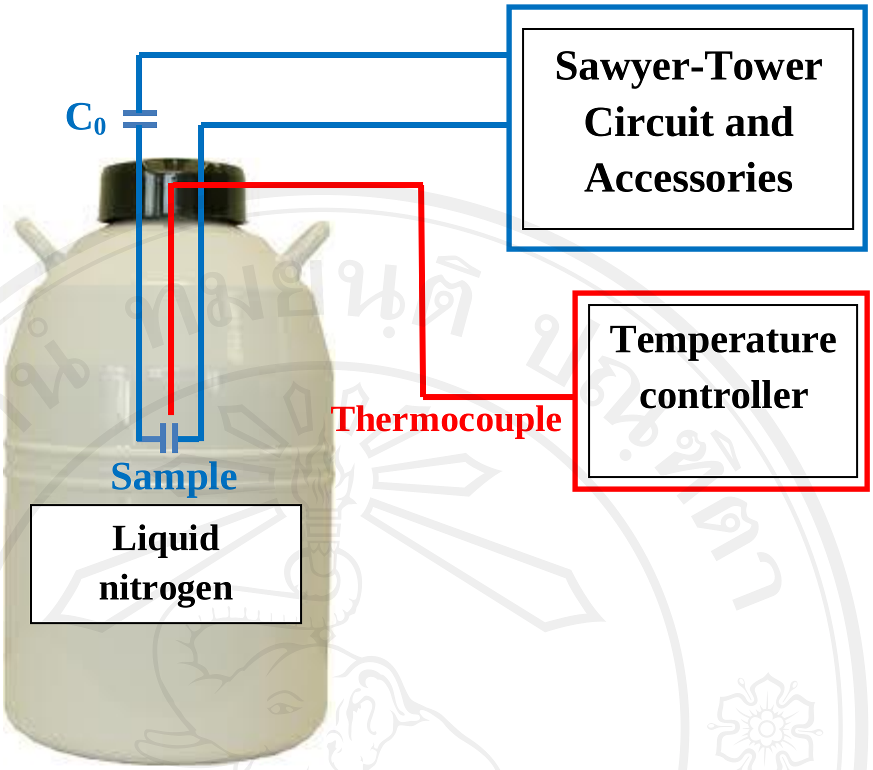

Figure 3.9 Schematic of the experimental setup for various temperature investigations (a) setup for high temperature investigation (T > 25 °C), (b) setup for middle low temperature investigation (-60 °C ≤ T ≤ 0°C) and (c) setup for the lowest temperature investigation (T < -60 °C)

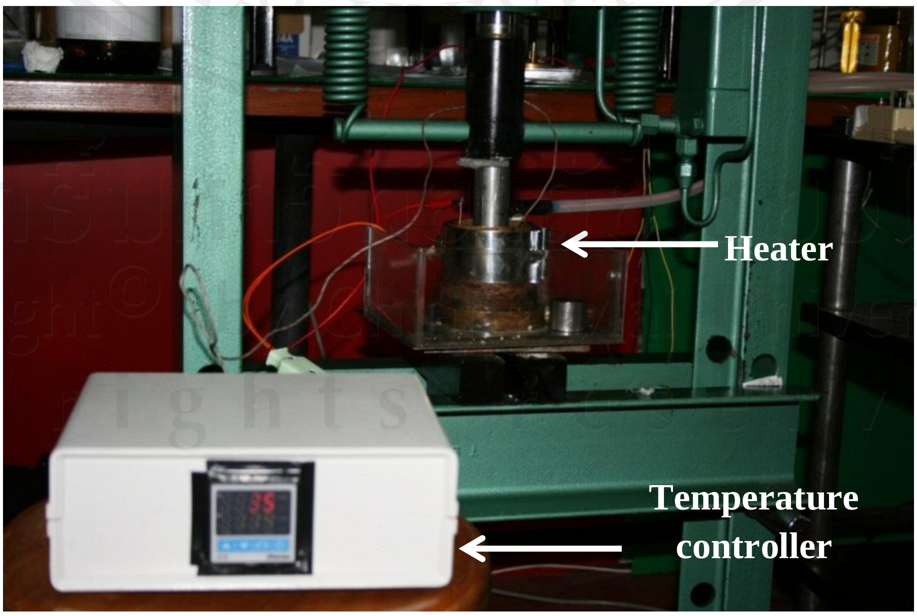

Figure 3.10 The setup for measuring ferroelectric hysteresis loop under influence of various temperatures

Similarly, the interested specimen is placed between the two alumina blocks in cylindrical brass cell and the electric field is applied to the specimen via the copper shims attached to the alumina blocks. During the measurements, the specimen is immersed in silicone oil to prevent high-voltage arcing during electrical loading.

Measurements are performed as a function of discrete temperature between -120 °C and 180 °C. For measurement of $T > 25$ °C, a desired temperature is first applied to the specimen and then electric field and frequency are applied respectively. In case of measurement of -60 °C $\leq T \leq 0$ °C, dry ice is used to fill in base surrounding cylindrical brass cell to cool down the temperature of specimen. A desired temperature can be obtained by adjustment amount of dry ice. Finally for the case of $T < -60$ °C measurement, dry ice cannot provide the coolness reaching such low temperatures, so liquid nitrogen is chosen to provide low temperature enough. A desired very low temperature can be obtained and adjusted by the distance between the liquid nitrogen surface and the specimen hanged in the liquid nitrogen container.

The ferroelectric hysteresis (*P-E*) loops are recorded with various frequencies and field amplitudes at discrete temperature. The electric field is applied to the specimen by a high voltage ac amplifier (Trek 610D) with the input sinusoidal signal from a function generator (HP 3310A). The developed ferroelectric hysteresis (*P-E*) loops are recorded by a digital oscilloscope (HP 54645A, 100 MHz) on discrete frequency and electric field at each constant temperature. The ferroelectric parameters are obtained after a total of 20 cycles of the electric field application to average out the noise deformation.

The measurement steps for temperature-dependent hysteresis properties investigation can be described as follows:

1. Specimen is placed between the two alumina blocks attached copper shims and immersed in silicone oil brass.
2. The desired temperature (by heating or cooling) is first applied to the specimen and then field amplitude and frequency are applied respectively.
3. At a constant desired temperature, when field amplitude is applied until reaching desired value, then frequencies are applied and varied as discrete value. The developed hysteresis (*P-E*) loops are recorded by picoscope program interfaced on computer.
4. When all (*P-E*) hysteresis loops obtained from varying discrete frequency over interested range at constant field amplitude and temperature are completely recorded, then applied field amplitudes are varied as discrete value over range of interest which each fixed discrete field amplitude, frequencies are varied following previous steps. *P-E* hysteresis loops are recorded for all variations.
5. When variations of frequency and field amplitude and recording of all developed *P-E* hysteresis loops at constant temperature are completed, then temperatures are changed and experimental steps of 2-4 are repeated again until accomplishing over temperature range of interest.
6. All steps above are used for both BT single crystals and BT bulk ceramics.

7. The information obtained is subsequently used to investigate the dependence of the dynamic hysteresis properties on the domain structure of ferroelectric materials.

Denote; Range of frequency and field amplitude depends on investigated specimens

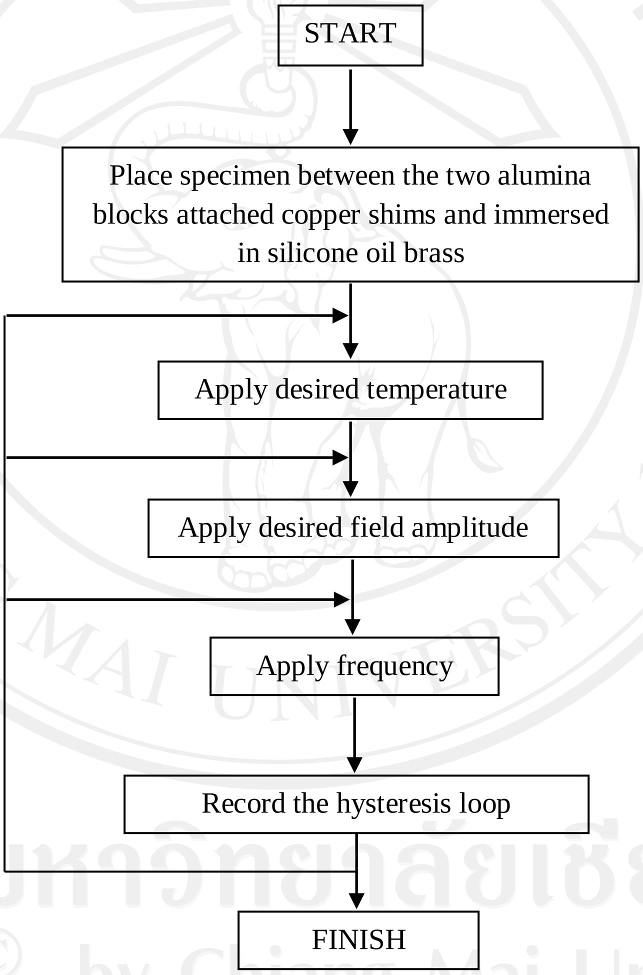

Figure 3.11 Flow chart of the dynamic hysteresis measurement for temperature dependence

3.2.2.1 BT bulk ceramics

Disc-shaped specimen synthesized by conventional mixed-oxide method of tetragonal $BaTiO_3$ bulk ceramic with 8 mm of diameter and 1 mm of thickness coated with silver paste at the top and bottom surfaces as an electrode is used. The ceramic has T_C = 124.5 ºC, ε_r at 100 kHz = 1143, tan δ at 100 kHz = 0.0477. The polarization-electric field (*P-E*) hysteresis loops are measured by using modified Sawyer–Tower circuit in conjunction with computer controlled oven over a temperature range of -120 ºC to 170 ºC. The system is capable of precise measurement of *P-E* behavior over the frequency range of 1 Hz - 100 Hz and electric field is applied from 0 to 15 kV/cm.

3.2.2.2 BT single crystals

The dynamic hysteresis (*P-E*) loops of tetragonal {001}-$BaTiO_3$ single crystal grown by the Remeika process [23,24] containing *a-c* domains [25,26] (triangular-shaped plates with 5 mm edge length and thickness of 0.5 mm) coated with silver paste at the top and bottom surface as an electrode are characterized by using a modified Sawyer-Tower circuit in conjunction with computer controlled oven over a temperature range of -120 ºC to 180 ºC with *f* covering from 1 to 300 Hz and E_0 from 0 to 15 kV/cm. Measurements are parallel to the tetragonal (001) direction.

3.2.3 The procedures for the dynamic hysteresis investigation with electric field-waveform

To study the influence of field-waveform on the ferroelectric properties, the sinusoidal and triangle waveforms are applied as electric field signal. The *P-E* hysteresis measurements are performed as a function of frequency and field amplitude at room temperature. The ferroelectric hysteresis (*P-E*) loops are recorded with various frequencies and field amplitudes. The electric field is applied to the specimen by a high voltage ac amplifier (Trek 610D) with the input sinusoidal/triangle signal from a function generator (HP 3310A). The developed ferroelectric hysteresis (*P*-*E*) loops are recorded by a digital oscilloscope (HP 54645A, 100 MHz). The ferroelectric parameters are obtained after a total of 20 cycles of the electric field application to average out the noise deformation.

The interested specimen is placed between the two alumina blocks in cylindrical brass cell and the electric field is applied to the specimen via the copper shims attached to the alumina blocks, as shown in Figure 3.12. During the measurements, the specimen is immersed in silicone oil to prevent high-voltage arcing during electrical loading.

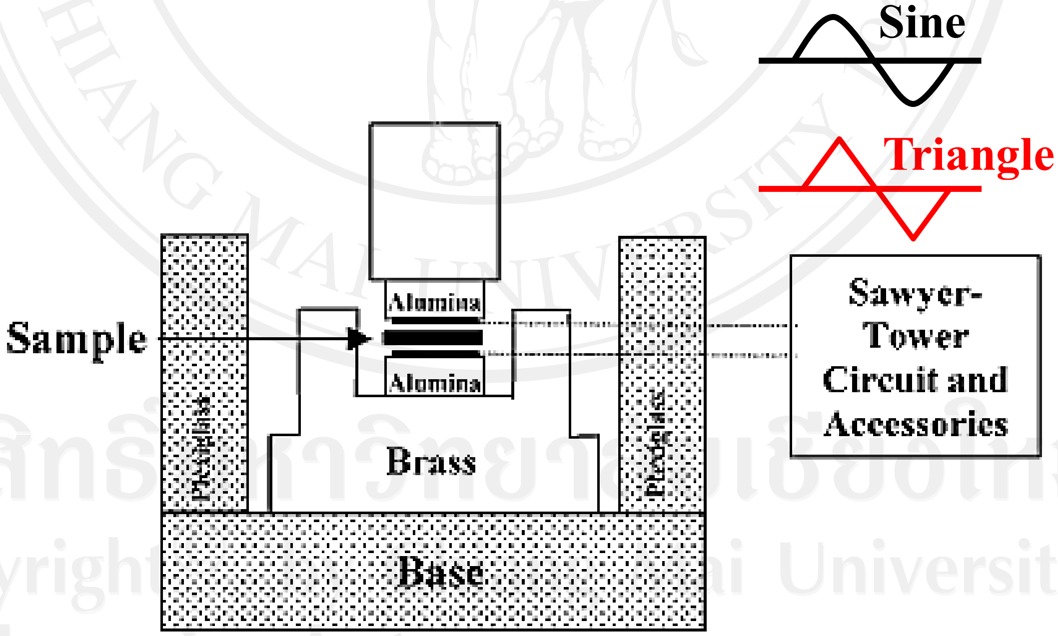

Figure 3.12 Schematic of the experimental setup for field-waveform dependence investigations.

The measurement steps for waveform-dependent hysteresis properties investigation are described as follows:

1. Specimen is placed between the two alumina blocks attached copper shims and immersed in silicone oil brass.
2. The desired electric field (sinusoidal/triangle) is applied to the specimen with frequency within range of interest.
3. At a constant desired electric field, frequencies are varied as discrete value and then the developed hysteresis (*P-E*) loops are recorded by picoscope program interfaced on computer.
4. When all (*P-E*) hysteresis loops obtained from varying discrete frequency in interested range at constant field amplitude are completely recorded, then applied field amplitudes are varied as discrete value within range of interest which each fixed discrete field amplitude, frequencies are varied following previous steps. Polarization hysteresis loops are recorded for all variations.
5. All steps above are used for all waveform investigations.
6. The information obtained is subsequently used to investigate the dependence of the dynamic hysteresis properties on the domain structure of ferroelectric materials.

Denote; All steps above are employed identically for both cases of sinusoidal and triangle waveform applications.

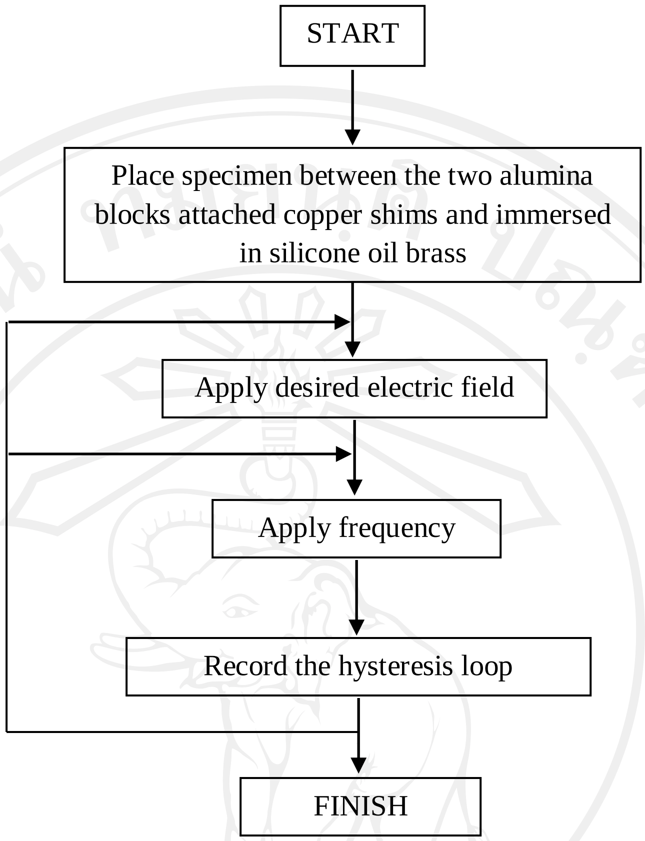

Figure 3.13 Flow chart of the dynamic hysteresis measurement for waveform-dependent investigation

0.7PMN-0.3PT single crystals

Commercial 0.7Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.3$PbTiO_3$ [0.7PMN–0.3PT] single crystal (IBULE PHOTONICS, Inc.) of square shape 5 x 5 mm^2 and thickness 0.65 mm coated with silver paste at the top and bottom surfaces as an electrode is investigated at room temperature (25 °C). The polarization-electric field (*P*-*E*) hysteresis loops are conducted by using a modified Sawyer–Tower circuit in conjunction with computer controller. The system is capable of precise measurement of *P*-*E* behavior over the frequency range of 1 Hz - 200 Hz. The electric field up to 15 kV/cm is applied on specimen by using a high voltage AC amplifier (Trek 610D) with the input of sinusoidal or triangle waveform generated by function generator (HP 3310A). The *P*–*E* loops are recorded by using digital oscilloscope (HP 54645A, 100MHz) after 20 sampling cycles.