CHAPTER 3

Experimental Procedure

3.1 Preparation of modified $PbTiO_3$ ceramics

3.1.1 Preparation of $Pb_{1-x}La_xTi_{1-x/4}O_3$ ceramics

The conventional powder processing technique was used to prepare La^{2+}-modified $PbTiO_3$ ceramics. Starting raw materials were oxides such as PbO, La_2O_3 and TiO_2 as listed in table 4. They were weighed in a stoichiometric ratio as shown in table 5 and mixed in ball milling using ZrO_2 as grinding media and acetone as a solvent in a high density polyethylene bottle (HPDE) for 21 hrs. Solvent was removed by filtration and dried in the oven at 80°C for 2 hrs. The dried mixture was placed in an alumina crucible with sealing a cover by alumina paste to prevent PbO loss and calcined at temperature of 750°C for PLT compositions and 800°C for PCT compositions using a heating rate of 120°C/hr, for 2 hrs (see fig.11). The calcining temperature was determined by XRD analysis in section 3.1.3. After calcining, the powder was milled for 21 hrs, filtered and dried at 80°C for 4 hrs in an oven. Powder was sieved through a 100 mesh screen and pressed to form disks of 15 mm. diameter using uniaxial hydraulic press with a pressure of 64 MPa. by pressing at 196 MPa (2000 kg/cm^3) in a Cold Isostatic Press (CIP) for 5 min. Specimens were weighed for determining the weight loss. The specimens were then placed in a closed alumina crucible, using the powder of the same composition as specimens as lead source. Specimens were heated at 600°C for 1 hr at a heating rate of 60°C/hr to remove organic matter and then

increased temperature to 1200°C with a heating rate of 240°C/hr and soaked for 2 hrs. The specimens were cooled in the furnace with a heating rate of 300°C/hr (see fig.12). The scheme for the preparation of $Pb_{1-x}La_xTi_{1-x/4}O_3$ ceramics is shown in fig. 13.

Electrical properties such as dielectric constant (K') , dielectric loss (D) and the P-E hysteresis loop were examined using Impedance Analyzer and a Radient Technologies RT6000HVS Ferroelectric Test system. Microstructures were determined using a JEOL scanning electron microscopy (SEM). The weight loss and shrinkage were measured for calcination and sintering specimens. X-ray diffraction (XRD) was used to determined c/a ratio and crystal structure. The sample preparation procedure and characterization are described in section 3.2.

3.1.2 Preparation of $Pb_{1-x}Ca_xTiO_3$ ceramics

PbO, $CaCO_3$ and TiO_2, starting materials as listed in table 4, were weighed in a stoichiometric composition as shown in table 6. The sample preparation and characterization procedure were the same that of $Pb_{1-x}La_xTi_{1-x/4}O_3$ ceramics but the calcining temperature was at 800°C.

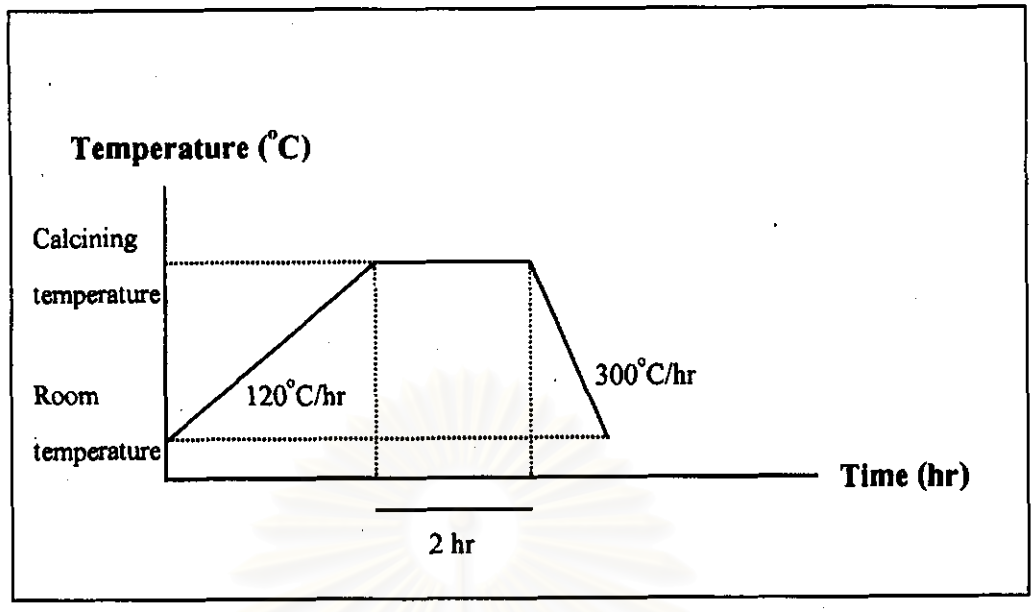

Fig. 11 The scheme of calcination profile

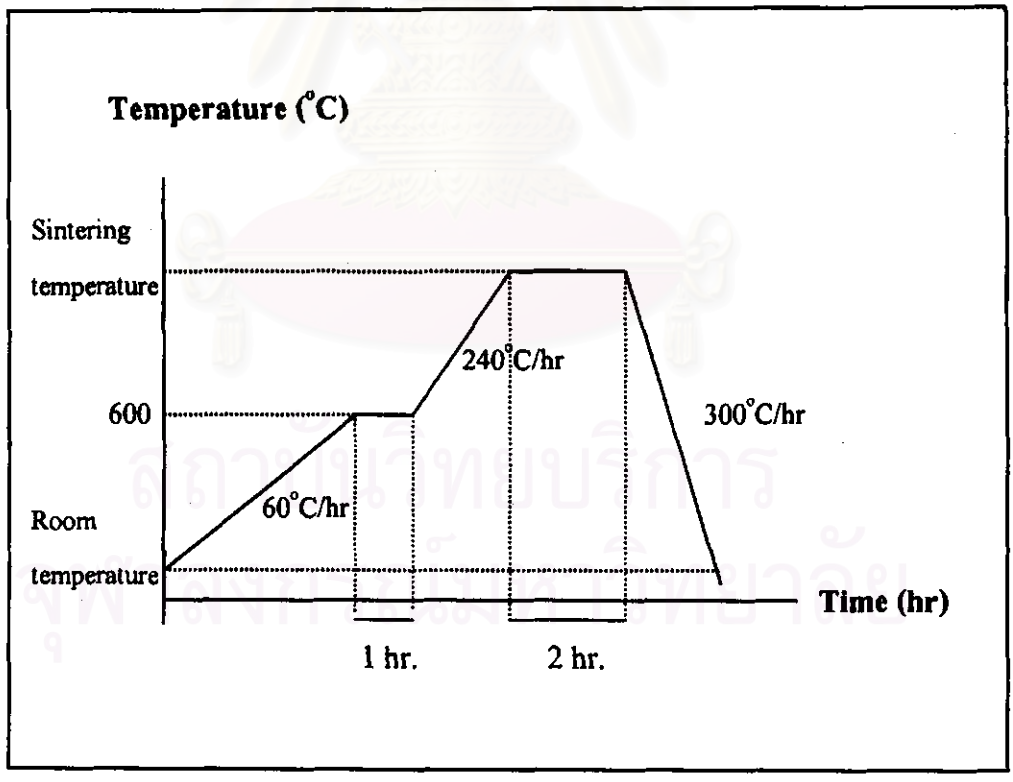

Fig. 12 The scheme of sintering profile.

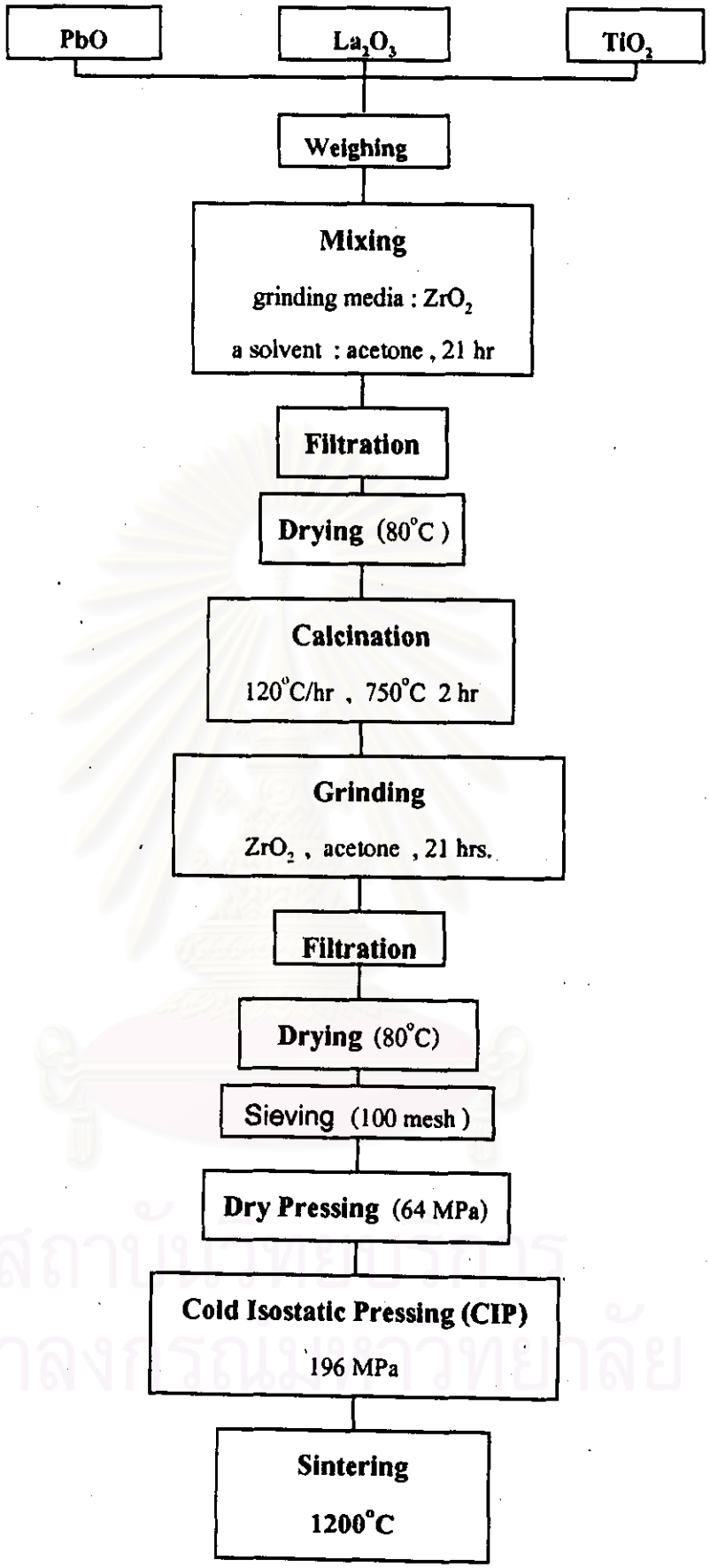

Fig. 13 The scheme for the preparation of $Pb_{1-x}La_xTi_{1-x/4}O_3$ ceramic

Table 4 Raw materials used in preparing the samples

Raw materials	Chemical supplier	Purity
Lead(II) oxide (PbO)	AnalaR	99%
Titanium dioxide (TiO_2)	Fluka Chemika	>99%
Calcium carbonate ($CaCO_3$)	MAY&BAKER LTD.	>98.5%
Lanthanum oxide (La_2O_3)	Fluka Chemika	>99.98%

Table 5 The stoichiometric ratio of $Pb_{1-x}La_xTi_{1-x/4}O_3$ ceramics

Unit formula	x	Molecular wt.	Molar ratio		
			PbO	La_2O_3	TiO_2
$PbTiO_3$, PT	0	223.19	0.738	-	0.262
$Pb_{0.95}La_{0.05}Ti_{0.9875}O_3$, PL5T	0.05	299.08	0.7089	0.0273	0.2638
$Pb_{0.90}La_{0.10}Ti_{0.975}O_3$, PL10T	0.10	295.06	0.6807	0.0553	0.2640
$Pb_{0.85}La_{0.15}Ti_{0.9625}O_3$, PL15T	0.15	291.05	0.6518	0.0840	0.2642
$Pb_{0.80}La_{0.20}Ti_{0.95}O_3$, PL20T	0.20	287.04	0.6220	0.1136	0.2644

Table 6 The stoichiometric ratio of $Pb_{1-x}Ca_xTiO_3$ ceramics

Unit formula	x	Molecular wt.	Molar ratio		
			PbO	$CaCO_3$	TiO_2
$Pb_{0.95}Ca_{0.05}TiO_3$, PC5T	0.05	296.93	0.714	0.017	0.269
$Pb_{0.90}Ca_{0.10}TiO_3$, PC10T	0.10	290.78	0.690	0.035	0.275
$Pb_{0.85}Ca_{0.15}TiO_3$, PC15T	0.15	284.62	0.667	0.052	0.281
$Pb_{0.80}Ca_{0.20}TiO_3$, PC20T	0.20	278.47	0.641	0.072	0.287
$Pb_{0.70}Ca_{0.30}TiO_3$, PC30T	0.30	268.15	0.581	0.114	0.305

3.2 Reaction analysis for determination of the calcining temperature

X-ray diffraction (XRD) was used to determine the suitable calcining temperature

3.2.1 Determining the calcining temperature of $Pb_{1-x}La_xTi_{1-x/4}O_3$ powder

$Pb_{0.95}La_{0.05}Ti_{0.9875}O_3$ was a selected composition used to examine the calcination condition. Regarding to a process described in section 3.1.1, the dried powder was heated to 300°C to 800°C and maintained at that temperature for 1 hour. The samples were ground in a mortar, packed in an aluminum sample holder and examined by Shimadzu X-ray diffractometer XRD-6000 using CuK_α radiation operating at 30 kV and 40 mA. The data were collected in the range of 2θ 20-70°. The optimum temperature could be obtained but the batch of this analysis (5 gms.) was less than the real batches for this research (50 gms). The soaking time of the real batches was increased to 2 hrs and a phase was reexamined after calcining.

3.2.2 Determining the calcining temperature of $Pb_{1-x}Ca_xTiO_3$ powder

Calcination of the stoichiometric of $Pb_{0.95}Ca_{0.05}TiO_3$ composition was investigated in a similar manner to PLT. The mixed powder was heat-treared for 2 hrs at temperatures ranging from 750°C to 850°C.

3.3 Characterization of $Pb_{1-x}La_xTi_{1-x/4}O_3$ and $Pb_{1-x}Ca_xTiO_3$ ceramics

3.3.1 Physical Characterization

3.3.1.1 Weight loss and shrinkage after calcination and sintering

The weight loss was determined from the weight before and after calcination and sintering using the following equation

$$\% \text{ weight loss} = \frac{(W_b - W_a)}{W_b} \times 100$$

where W_b = the weight before calcination or sintering (gms)

W_a = the weight after calcination or sintering (gms)

The firing shrinkage was examined from the diameter and thickness of samples before and after sintering. Its value could be obtained from this equation

$$\% \text{ firing shrinkage} = \frac{(D_b - D_a)}{D_b} \times 100$$

where D_b = the diameter or thickness before sintering (mm.)

D_a = the diameter or thickness after sintering (mm.)

3.3.1.2 Microstructure

The microstructure of sintering samples was examined using a JEOL JSM-T330A Scanning Electron Microscope (SEM). Samples were polished in the cross-section and thermally etched at 1100°C which was lower than the sintering temperature (1200°C) using a similar heating rate as the sintering. Carbon paint was applied to stick the samples on the stubs. Samples were sputter-coated with gold to prevent charging in the microscope prior to examination.

3.3.1.3 X-ray Diffraction Analysis

The X-ray diffraction analysis is used to examine the crystal structure and the lattice parameter. Calcined powders were ground , packed into aluminum sample holder and examined in a Shimadzu X-ray diffractometer XRD-6000 using CuK_{α} radiation operating at 30 kV. and 40 mA. The data were collected with the different scanning rates in three ranges of 2θ, 20-40° with 1 deg/min, 40-50° with 0.5 deg/min and 50-70° with 1 deg/min. Slower speed was used in the range of 2θ for calculating a lattice parameter. Silicon was mixed into the powder as an internal standard. The sintered compositions were selected to examine the phase. However, the pellets were used for this analysis.

The lattice parameter of the tetragonal structure can be expressed by

$$\frac{1}{[\, d_{(h,k,l)} \,]^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

where d (h,k,l) is the d spacing of the h, k, l planes

a, c are the lattice parameters

Lattice parameters of a tetragonal phase were calculated from (100), (001), (200) and (002) peaks after a correction from peak shifts compared to those of Si standard.

3.3.2 Electrical Characterization

Prior to electrical measurements the specimens were polished into the thickness of 0.7 mm. and electroded by gold sputtering (Eiko IB-3). The capacitance (C), dielectric loss (D) and the polarization vs electric field (P-E) response were measured at room temperature. In addition, the Curie temperature of some compositions which performed the highest remanent polarization was determined.

3.3.2.1 Dielectric constant (K') and Dielectric loss (D) at room temperature

The capacitance, C , and dielectric loss , D , for each specimen were examined at room temperature using an HP 4192 impedance analyzer at different frequencies 10 , 100 kHz. and 1 MHz , respectively. The dielectric constant was calculated from the above measurement according to the formula:

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A}$$

where ε_0 = permittivity of free space (8.85×10^{-12} Fm^{-1})

A = specimen area or electrode area (m^2)

t = specimen thickness (m)

C = specimen capacitance (F)

3.3.2.2 Dielectric constant (K') and Dielectric loss (D) versus temperature

Specimens were placed on the sample holder as shown in fig. 14 for measurement of dielectric constant and dielectric loss. All data were recorded every 5°C from room temperature to 350°C. A schematic of apparatus used for this measurement showed in fig.15.

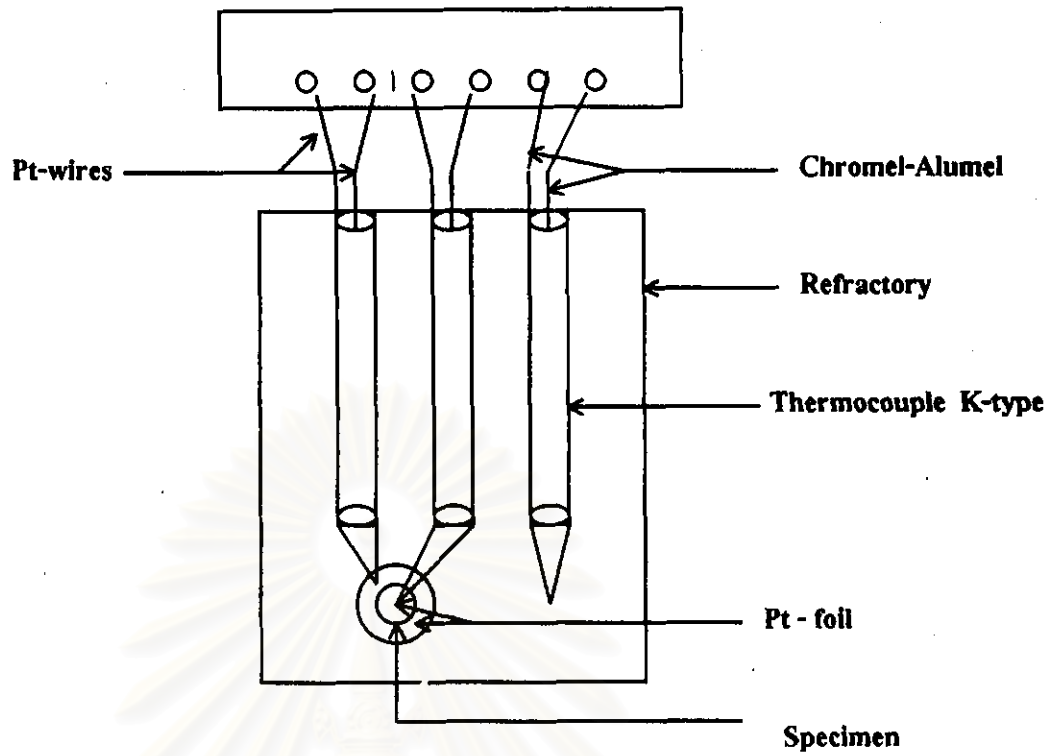

Fig.14 sample holder for the capacitance and dissipation factor measurement

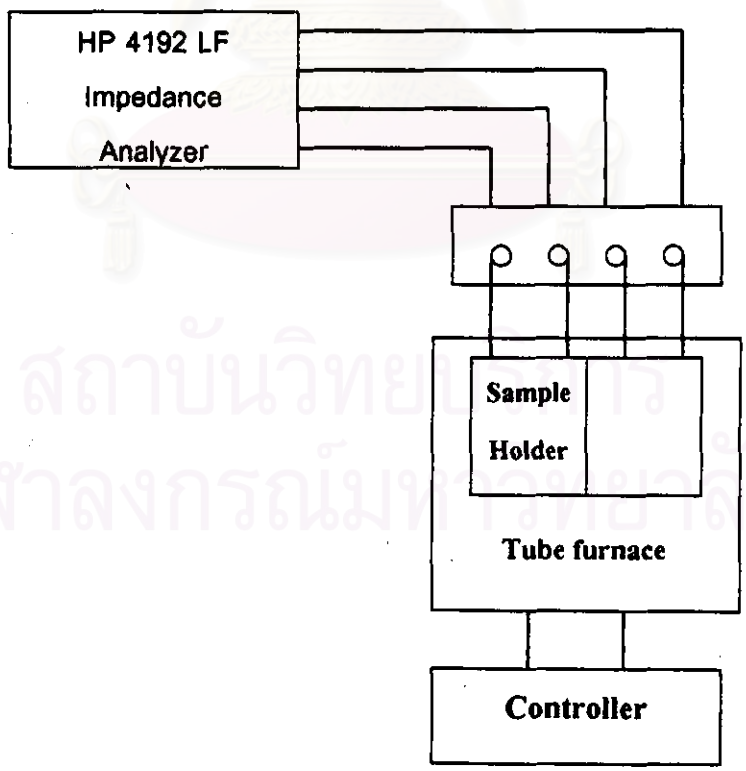

Fig. 15 The Scheme of apparatus used for the capacitance and dissipation factor

3.3.2.3 The polarization-electric field (P-E) response

The polarization-electric field (P-E) response of PCT and PLT systems were examined by using a standard ferroelectric test system (Model RT6000HVS, Radiant Technologies, Albuguerque, NM 87106) with the Virtual Ground measuring system at a frequency of 60 Hz. The measurement technique of the Virtual Ground mode is similar to the Sawyer Tower system which is shown in fig 16. For the Sawyer Tower system, the specimen corresponds to a capacitor , C_x ,of which its electrodes are connected with a standard capacitor , C_o. When the AC current is applied to the sample, C_x , the voltage drop across of both capacitors, C_x and C_o can be collected by an oscilloscope as V_x and the voltage across C_o measures the charge stored on the test sample which is displayed as V_y . Since $V_y = q/C_o$ where q is the charge on the sample, the trace on the oscilloscope expresses the relationship between the charge produced on the sample (referred to on the x-axis) and voltage applied to the specimen (referred to as the y-axis). However, this measurement is not supplied in the high voltage mode. In the Virtual Ground mode system, the high voltage can be measured using the transimpedance amplifier connected parallel to a standard capacitor , C_o (see fig 17) so that the charge of high voltage can be integrated. The capacitance value of a standard capacitor is not large for high voltage (Q = V/C) and the reliable data can be collected.

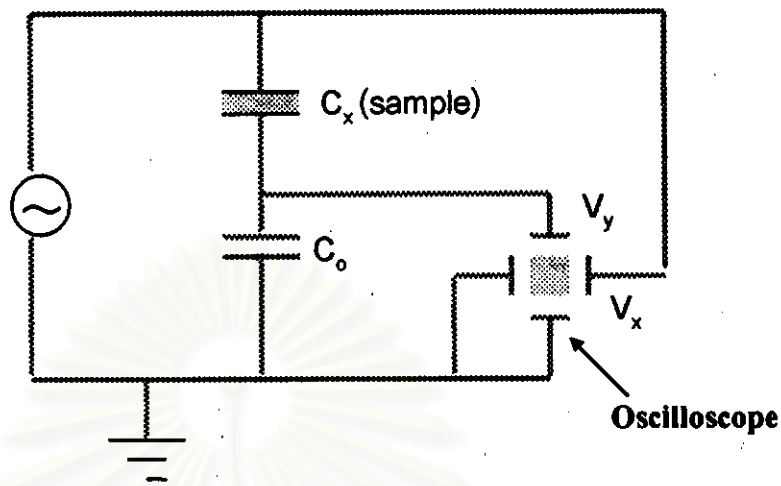

Fig. 16 The Sawyer Tower circuit

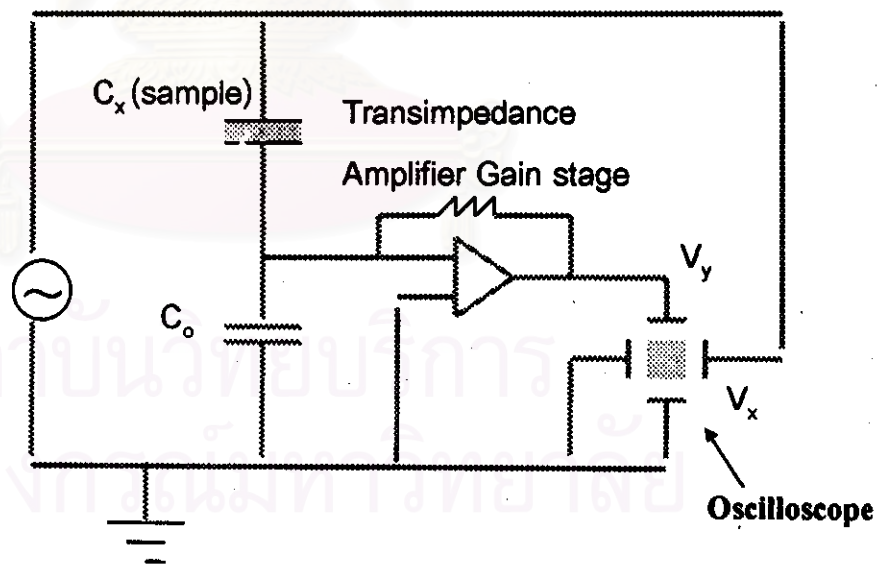

Fig. 17 The Virtual Ground Mode Circuit