

CHAPTER 3

EXPERIMENTAL METHODS AND PROCEDURES

3.1 Fabrication of PZT Powders

Earlier studies [10-11] revealed that the PZT properties are affected by their microstructures which partly depend on size and homogeneity of the starting powders. Generally, those conventional methods [24] using ball milling of the constituent oxides have the difficulty in controlling the powder size, particle size distribution and homogeneity of the PZT powders. However, fine, homogeneous PZT particles can be obtained via chemical processes [25,26,27,31,32]. Ceramics produced from these powders often yield encouraging piezoelectric and dielectric properties. The PZT ceramics produced via the chemical processes usually require very high purity (> 99.9 %) and high cost chemicals which are not appropriate for large scale production.

To focus in the powder preparation by using the low grade starting powder, the modified spray dry technique was studied in this work. Moreover, the conventional mixed oxide method was also fabricated for comparison.

3.1.1 Preparation of PZT powder by spray drying technique

The low-price chemicals used in this work are solutions of lead nitrate ($\text{Pb}(\text{NO}_3)_2$, 99 % by weight), zirconyl nitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ~27 % of Zr by weight and tetraisopropyl orthotitanate ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$, ~99 % by weight). The molar ratio of those solutions was kept at 1:0.52:0.48 which is corresponding to the crystal phase of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$. By following the work done by Tunkasiri [98], the aqueous solutions of $\text{Pb}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were firstly mixed. Then the mixture of the $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ solution and strong nitric acid (HNO_3 , pH ~ 1) was gradually added into the previously mixed solution. In order to stabilize the metals in the solution, the hydrogen peroxide (H_2O_2) was added. Aqueous ammonium solution was then slowly added to control the pH of the mixture solution. In order to obtain manganese-doped PZT ceramics for reducing the loss angles and increasing the resistivity [26], a solution of manganese chloride (MnCl_2) was admixed. The solution was then fed into the nozzle of a spray dryer at an operating temperature of 130 °C to obtain fine granules. The granules were subsequently calcined at 500, 600, 700, 800 and 850 °C for 1 hour. An X-ray diffractometer (XRD, Siemens) was employed to study the phase evolution. The microstructures of the powders and ceramics were investigated using SEM. The purity of the PZT particles was observed using TED and EDS. The thermal characteristics of PZT powders were studied using DTA and TG.

In order to obtain Mn-doped PZT ceramics, the powder that was calcined at 700 °C for 2 hours was pressed (3500 psi) into circular disks with approximately 2.5 cm in diameter and 1 mm in thickness. Polyvinyl alcohol (PVA) was used as a binder. The

samples were sintered at 900, 1000, 1100, 1200 and 1250 °C for 1 hour respectively, with the heating rate of 100 °C/h. Then the samples were held at 500 °C for 30 mins for binder removal before heating up to their sintering temperatures. The XRD was used to study the phase formation and SEM was used to observe the surface microstructure of the sintered ceramics.

Silver paste was applied to the samples for electrical contact. Poling was carried out at 130 °C in a stirred silicone oil bath using a field of 18 kV cm⁻¹ for about 5 min. The dielectric constant (ϵ_r), loss factor ($\tan\delta$) and planar coupling coefficient (k_p) were measured using an impedance/gain-phase analyzer (LCZ) (Model 4276, Hewlett Packard). The piezoelectric coefficient (d_{33}) was measured using a piezo- d_{33} meter (Model CADT Berlincourt). Relative densities of the prepared ceramics were also measured using Archimedes' principle. X-ray diffraction and electron microscopy were employed to analyse the ceramic samples. The schematic of preparation of PZT powder prepared by spray drying technique is shown in Figure 3.1.

3.1.2 Preparation of PZT powder by mixed oxide method

PZT ceramics with the morphotropic phase boundary (Zr/Ti = 52/48) incorporated with the dopant were prepared via the conventional solid-state-reaction route. Lead oxide (PbO ~ 99%, Fluka), zirconium oxide (ZrO₂ ~ 99%, Fluka), titanium dioxide (TiO₂ ~ 99%, Reidel) and manganese oxide (MnO₂ ~ 99%, Reidel) were employed as precursors. They were weighed according to appropriate molar fractions,

mixed and wet milled (in ethanol) for 24 h in the zirconia grinding media. The mixtures were dried and calcined at 850 °C. The mixtures were then reground and formed into circular disks with diameter of 15 mm. and thickness of 2.5 mm. 2 wt% polyvinyl alcohol (Fluka) was employed as binder. The samples were sintered at 1200 °C with heating/cooling rate of 5 °C/min in a close alumina crucible with a lead atmosphere provided by lead zirconate (PZ) powder. The polished samples were electroded and poled in an electric field of 10 kV/mm for 30 min in silicone oil at 120 °C. The planar coupling coefficient (k_p), dielectric constant (ϵ_r), loss angle ($\tan \delta$) were measured (using Hewlett Packard 4192 LF impedance analyzer and 16048 A test lead). An X-ray diffractometer (XRD, Philips) and a scanning electron microscope (SEM, Philips XL 30 ESEM) were employed to study phase evolution and microstructure of the samples, respectively. The schematic of preparation of PZT powder prepared by mixed oxide method is shown in Figure 3.2.

3.1.3 Preparation of PZT powder by modified method

In this method, the PZT powder prepared by using spray drying technique was mixed with MnO_2 -dopant by wet ball milling. The processing is the same as the conventional mixed oxide method. The sprayed powder and MnO_2 -dopant were weighted and put into the plastic box with the zirconia grinding media. Thereafter, powder and dopant were then mixed for 24 h, dried and calcined, respectively. The ceramics were then fabricated and characterized in the same way of samples made from spray drying technique and mixed oxide method.

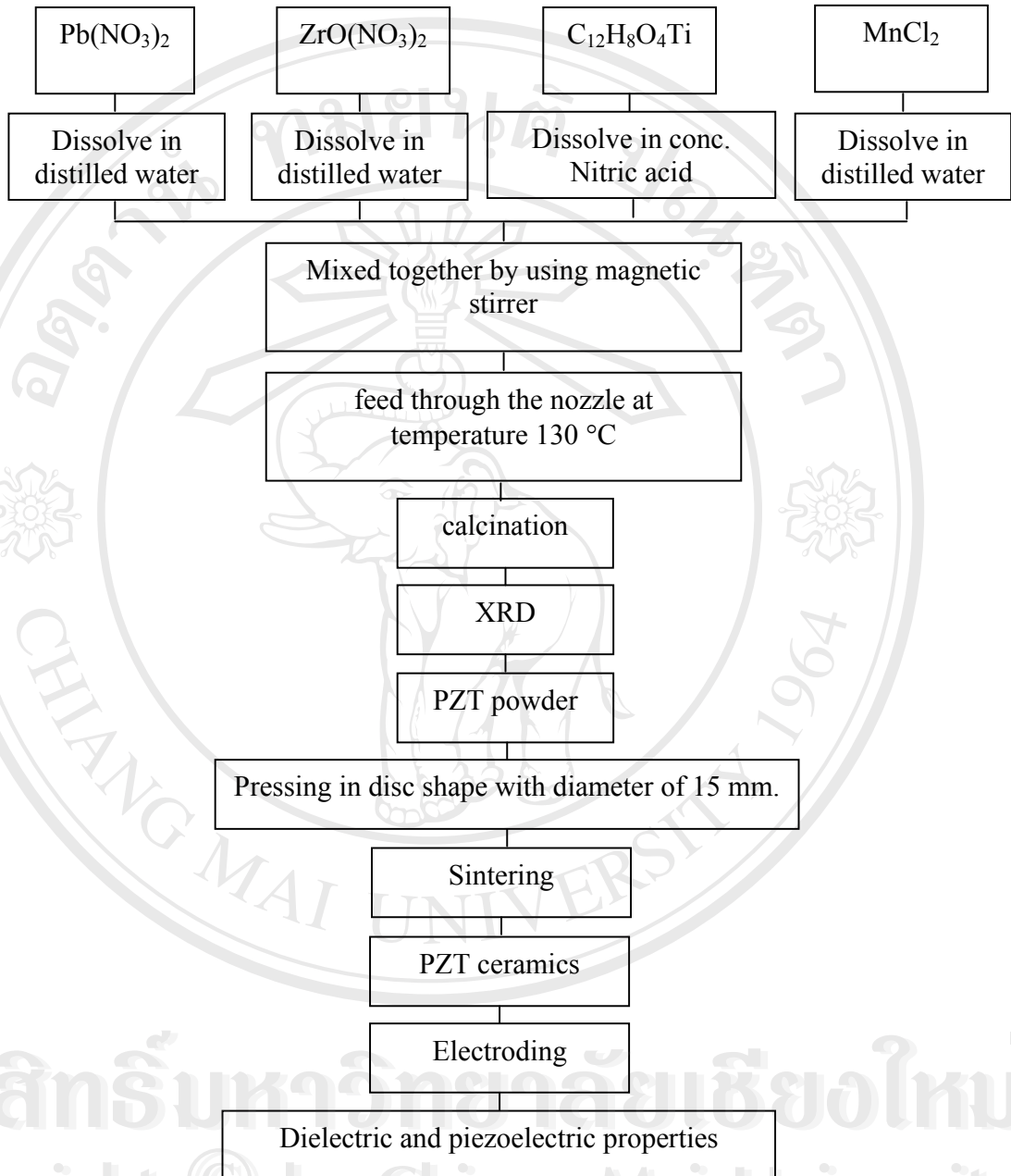


Figure 3.1 Schematic of preparation of PZT samples by using spray drying technique.

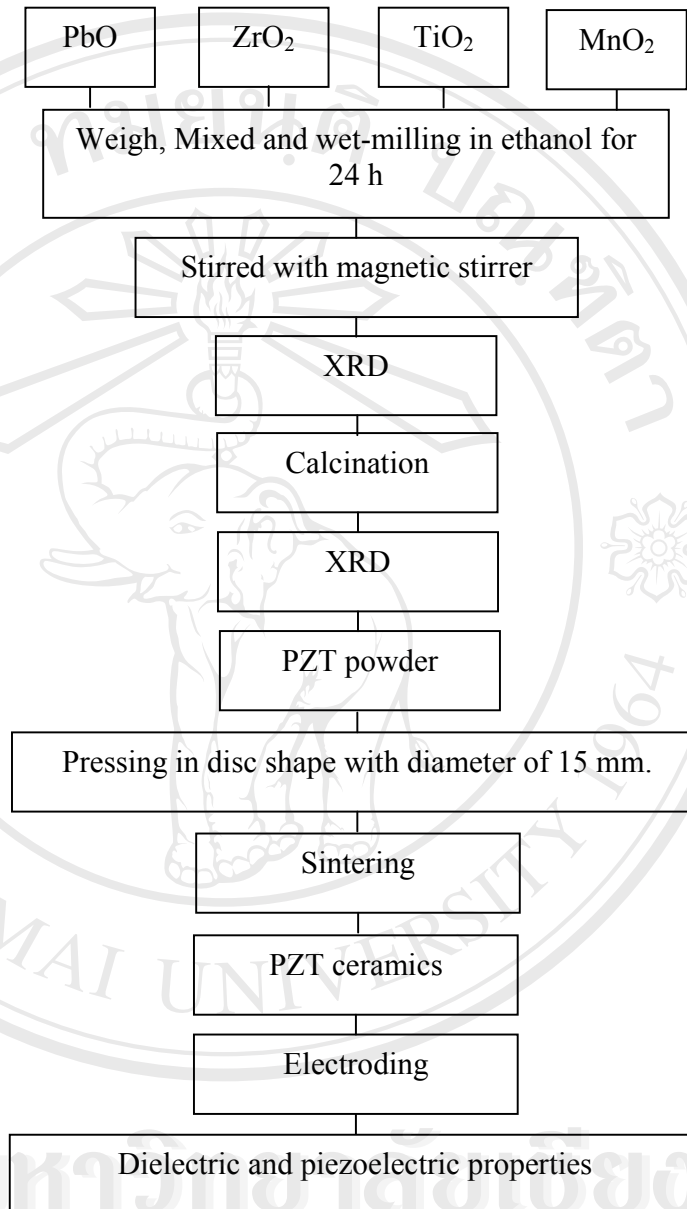
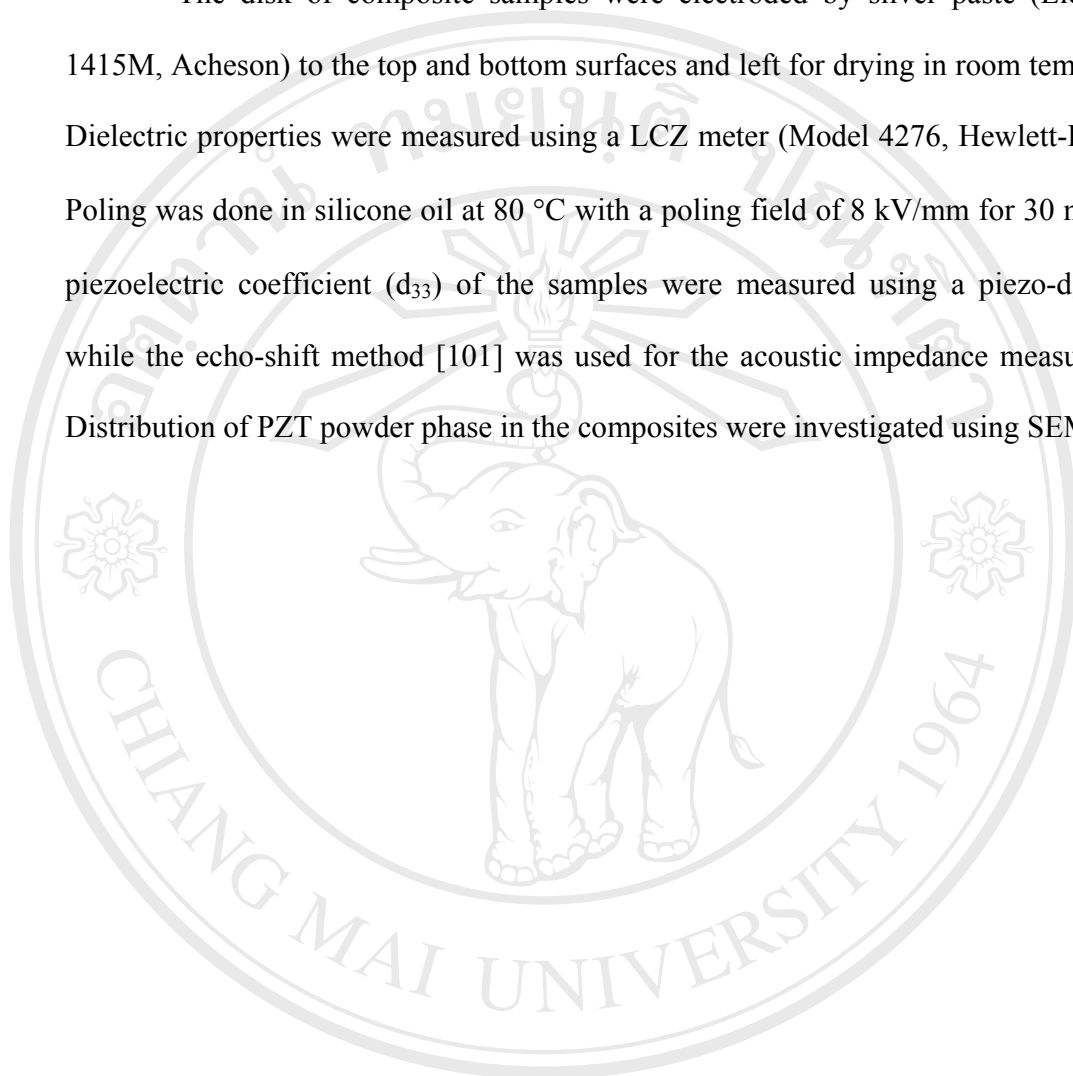


Figure 3.2 Schematic of preparation of PZT samples by using mixed oxide method.

3.2 Processing of 0-3 ceramic-polymer composites

Combination of 0-3 and 1-3 connectivities composites were produced based on dice and fill method [100]. Firstly, PZT powders obtained from mixed oxide method (particle size $\sim 4 \mu\text{m}$) and spray drying technique (particle size $\sim 1 \mu\text{m}$) were used as active phase and epoxy resin (Epofix, Strurer) was employed as passive polymer phase. Thereafter, 0-3 PZT/epoxy resin composites were fabricated by the suction technique. Details of the suction technique are described in Figure 3.3. PZT powders were put in a plastic syringe with a filter paper (Whatman) placed underneath. Epoxy resin was then poured into the syringe with PZT powders and resin was plugged in a flask partly filled with water, as shown in Figure 3.3 and suction was carried out using an air pump for enhancing the flow of the resin through the PZT powders. A filter (No.42) was used to prevent the powders flowing into the suction system. The samples were left for 2 days at room temperature, allowing them to settle. The samples in the syringe is now a 0-3 piezoceramic/epoxy resin composite, with about 1 cm. thick and 1.5 cm. in diameter. The sample was then diced using a diamond saw (series 15HC Diamond, Buehler) into squares of $0.35 \times 0.35 \text{ (mm}^2\text{)}$ to create a 1-3 connectivity pattern. Epoxy resin was then poured in again to fill up the spaces. The samples were left for 2 days to settle. These new samples are now a combined 0-3 and 1-3 ceramic/epoxy resin composite where each column (0-3 ceramic/epoxy resin) formed a 1-3 connectivity with the resin in the spaces. The composite sample was then taken out from the syringe and cut into disks with a thickness of 1 mm (Figure 3.4). The density of the samples was measured by the conventional Archimedes' method.

The disk of composite samples were electroded by silver paste (Electrodrag 1415M, Acheson) to the top and bottom surfaces and left for drying in room temperature. Dielectric properties were measured using a LCZ meter (Model 4276, Hewlett-Packard). Poling was done in silicone oil at 80 °C with a poling field of 8 kV/mm for 30 min. The piezoelectric coefficient (d_{33}) of the samples were measured using a piezo- d_{33} meter, while the echo-shift method [101] was used for the acoustic impedance measurements. Distribution of PZT powder phase in the composites were investigated using SEM.



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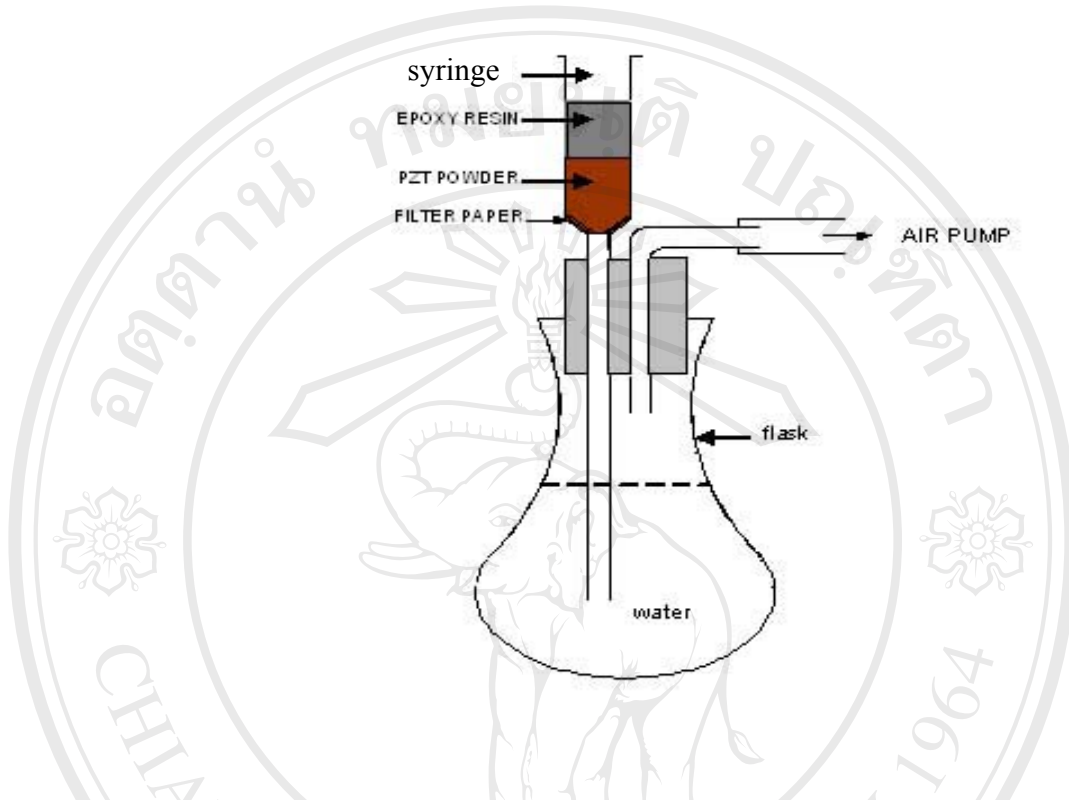


Figure 3.3 Schematic of the equipment to prepare 0-3 piezoceramic/epoxy resin composites. The PZT/powders and resin were filled in a syringe with a filter underneath. The syringe was plugged in a flask partly filled with water. Suction was carried out through an air pump.

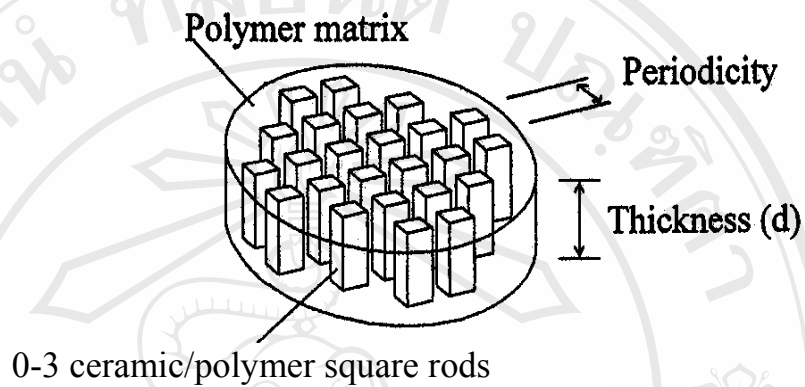


Figure 3.4 Schematic of photograph of (0-3) and (1-3) combined piezocomposite sample where polymer matrix = epoxy resin filled in the spaces to form the 1-3 connectivity with 0-3 ceramic/polymer rods (0.35×0.35 mm.) Thickness (d) = 1 mm., periodicity = 0.7 mm. (picture based on [7])

3.3 Characterization and Measurement Methods

3.3.1 Thermal Analysis

Thermal analysis, TA, involves the measurement of certain physical and chemical properties as a function of temperature. These are mainly enthalpy, heat capacity, mass and coefficient of thermal expansion. The main TA techniques are thermogravimetry (TG), which records the mass of a sample as a function of temperature or time and a differential thermal analysis (DTA), which measures the difference in temperature, ΔT , between a sample and an inert reference material as a function of temperature, DTA therefore detects changes in heat content. The temperatures should be the same until some thermal event, such as melting, decomposition or change in crystal structure, occurs, in which case the sample temperature either lags behind (if the change is endothermic) or leads (if the change is exothermic) the reference temperature.

3.3.2 Particle Size Analysis of PZT Powder

The particle size distribution of PZT powder was measured using a particle size analyzer and a scanning electron microscope. Each method will be described in the next subsections.

3.3.3 X-Ray Diffraction Analysis

The PZT powder was characterized by x-ray diffraction to determine the phase and interplanar spacing (hkl). X-ray diffraction examination was conducted using $\text{CuK}\alpha$ radiation through a Ni filter. The generator was operated at 30 kV and 20 mA. The XRD

line profiles of the calcined PZT powder were obtained over a 2θ range of 20° - 60° , with a step of 0.5 degree and 1 sec counting time. In order to study the phase evolution with temperatures, the powder prepared by using spray dry technique and mixed oxide method were fired at temperatures of 500°C , 600°C , 700°C , 800°C and 850°C , 2 hour each step. Moreover, the PZT ceramics were sintered at the temperature of 900°C , 1000°C , 1100°C , 1200°C and 1250°C for 2 hour. The result of XRD was compared with the JDPDS file in the database to examine the phase formation.

3.3.4 Scanning Electron Microscopy (SEM)

The particle size, shape and morphology of the PZT ceramic powder and the microstructure of composites were characterized using scanning electron microscopy (SEM). The samples were mounted on metal sample holders prior to coating with gold via r-f sputtering techniques. For PZT powders, they were dissolved in ethanol, shaken by ultrasonic bath, dropped the mixture on metal sample holder, left it dry in the air and then coated with gold.

3.3.5 Transmission Electron Microscopy (TEM)

The dislocations, stacking faults, antiphase boundaries and twin boundaries may be seen directly by using this technique. Moreover, by changing the relative position of the viewing screen, the diffraction pattern, rather than the image, of the specimen is seen and can also be photographed. The region of the sample that is chosen for imaging is controlled by an aperture placed in the intermediate image plane. This is particularly

important in examining polycrystalline materials that contain more than one phase. Furthermore, the quality of photographs may be improved by dark field imaging. In this experiment, only the beams diffracted from the particle of interest are allowed to recombine to form the image.

3.3.6 Energy Dispersive Spectroscopy

Some SEM and TEM instruments have the very valuable additional feature of providing an elemental analysis of sample composition. When a sample in the microscope is bombarded with high-energy electrons, many things can happen, including the generation of X-rays. The X-rays are characteristic emission spectra of the elements present. By scanning either the wavelength (wavelength dispersive, WD) or the energy (energy dispersive, ED) of the emitted X-rays, it is possible to identify the elements presented in the samples. With suitable calibration, quantitative elemental analysis may be made.

3.4 Property Measurement of the Composites

3.4.1 Density Measurement

The density of the composite sample was measured using the Archimedes principle. The polished composite samples were first weighed in the air (W_d). Then, they were heated in boiling water for 10 min. After that, the samples were weighed again in pure water to determine the wet weights (W_w) by suspending on a thin copper wire. The density was then calculated from the following formula

$$\rho = \left(\frac{W_d}{W_d - W_w} \right) \rho_{\text{water}} \quad (3.1)$$

The theoretical density of the composite was also calculated. The following equation was used to determine volume% of ceramic loading of the composites [58].

$$\rho_{\text{composite}} = (\text{vol}\% \text{ceramic}) \cdot \rho_{\text{ceramic}} + (\text{vol}\% \text{polymer}) \rho_{\text{polymer}} \quad (3.2)$$

3.4.2 Polarization of the Composites

The composites were polished to a thickness of 0.4-0.5 mm and electroded for poling with and air-dried silver paint (Archeson: ELECTRODAG 1415M). Guarded electrode was employed to avoid current shorting across the edges of the thin samples during the poling process. The electrodes were applied through a circle mask by the brush and allowed to dry at room temperature for 2 hours before poling.

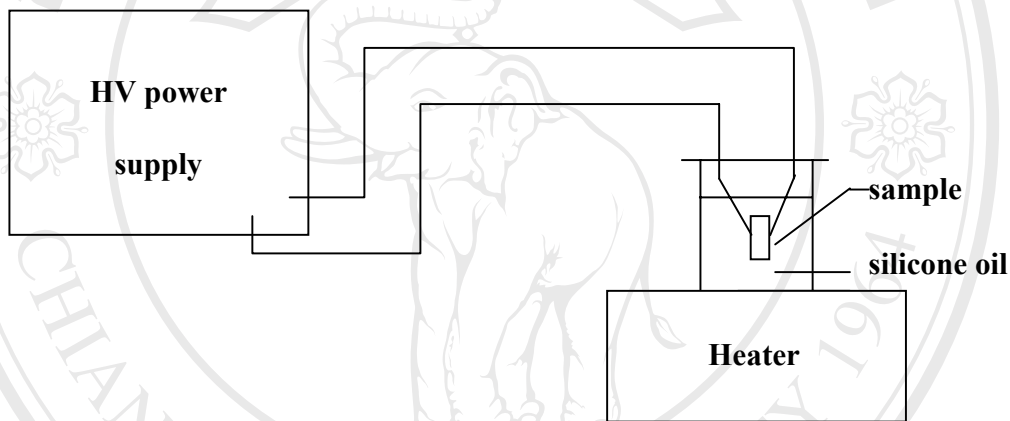


Figure 3.5 The poling apparatus.

Figure 3.5 shows a diagram of the poling apparatus which consists of a spring-loaded sample holder suspended in a temperature-controlled silicone oil bath and a dc high voltage generator. The voltage was applied stepwise, the specimen was held at a particular voltage for 3-5 minutes, and the field was then increased. This procedure minimized the possibility of dielectric breakdown and allowed higher fields to be applied. The maximum poling field was about 8-10 kV/mm at temperature of 80°C for 30 minutes.

3.4.3 Dielectric Properties

The capacitance (C) and dissipation factor ($\tan\delta$) of composites were measured at room temperature at a frequency range of 100-20,000 Hz using LCZ meter (Hewlett Packard : model 4276). The dielectric constant was determined from the equation,

$$\epsilon_r = \frac{Ct}{\epsilon_0 A} \quad (3.3)$$

where

C is the sample capacitance,

t is the sample thickness,

ϵ_0 is the permittivity of free space constant
(8.854×10^{-12} Farad per meter), and

A is the electroded area

3.4.4 Piezoelectric Properties

The piezoelectric charge coefficient (d_{33}) was measured dynamically using a d_{33} -Piezometer. The composite samples were put in the probes and the d_{33} values were read directly from meter display.

For the efficiency of conversion energy of PZT sample can be calculated from following equation :

$$k_p = \sqrt{\frac{2.5(f_a^2 - f_r^2)}{f_a^2} + 0.038} \quad (3.4)$$

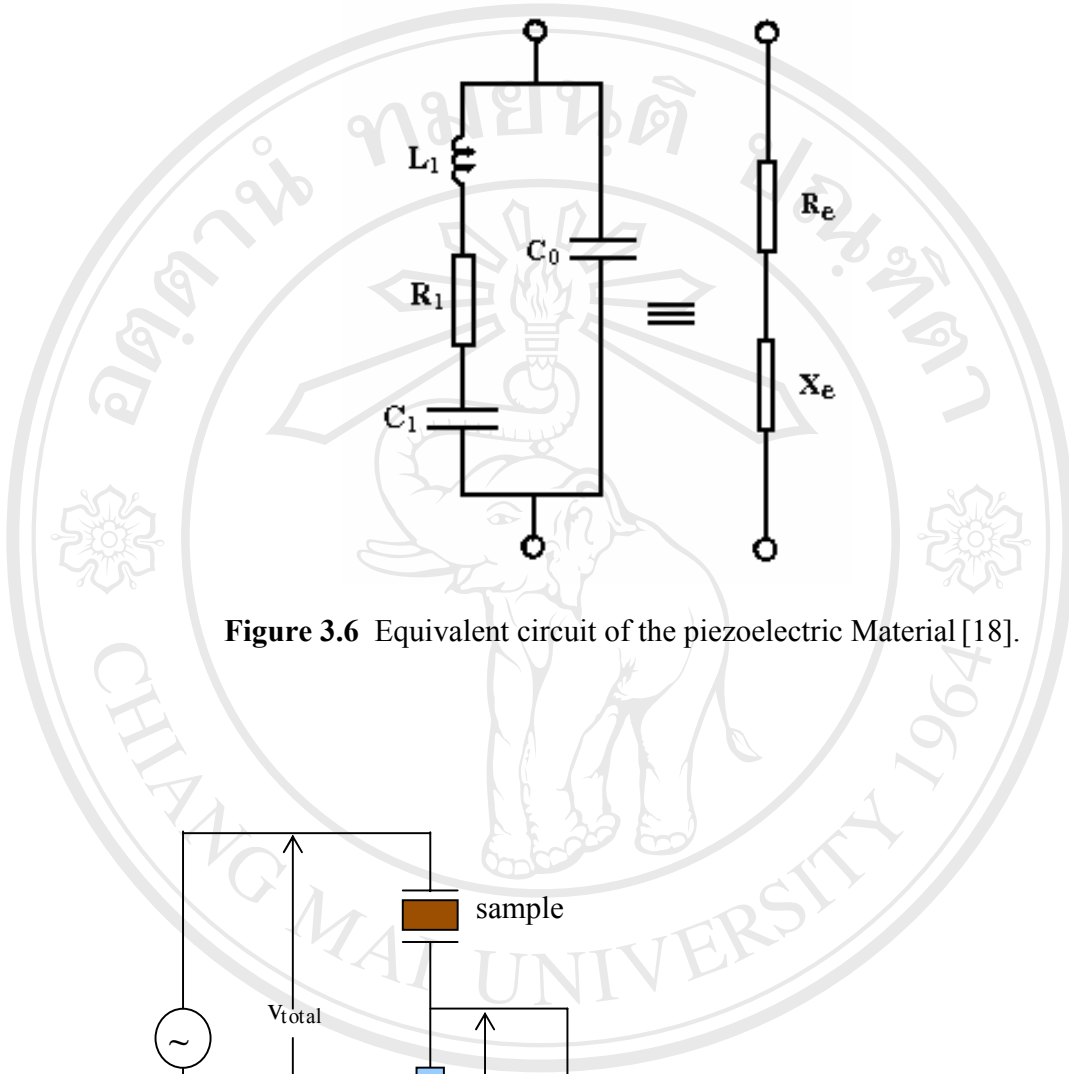


Figure 3.6 Equivalent circuit of the piezoelectric Material [18].

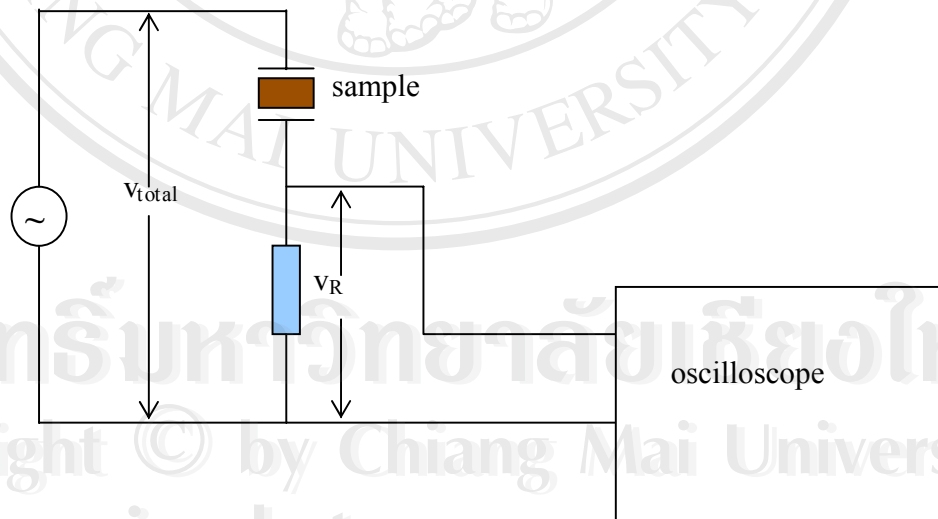


Figure 3.7 The circuit diagram for measuring of f_r and f_a .

3.4.5 Acoustic Impedance

It is well known that the piezoelectric ceramic materials such as PZT with high electromechanical coupling suffer from a severe disadvantage when operated with a low impedance load such as that of the human body or water [58]. The acoustic impedance of PZT is around 30 Mrayl while that of the tissues is 1.5 Mrayl. Thus, this value is an important parameter of transducer.

The acoustic impedance (Z) of a material is related to its mechanical properties by the equation

$$Z = c_L \rho = (K\rho)^{0.5} \quad (3.5)$$

where c_L is the longitudinal velocity in the material, ρ and K are the material's density and Bulk Modulus, respectively. The unit of Z is Mrayl (10^6 kg/sec.m^2) and K is N/m^2 .

The echo shift method [119] is used to measure the longitudinal velocity in the samples. The equipment is shown in Figure 3.8. The pulse signals which generated from pulse generator were transmitted passing through the sample and reflected at the surface of a stainless steel target back to a receiver. The time shift (ΔT) in the echo is determined using the phase analyzer. The velocity was then calculated using the equation

$$c_L = t/\Delta T \quad (3.6)$$

where t is the thickness of the samples.

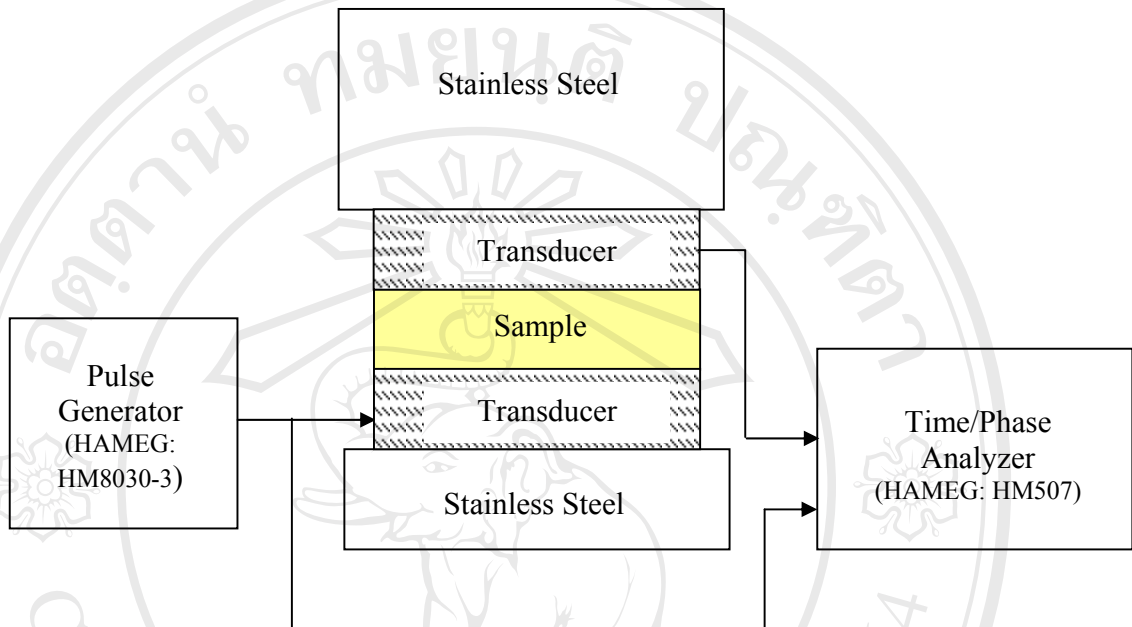


Figure 3.8 Diagram of the apparatus for echo shift measurement [119].