Chapter 3

Experimental work

Pb-based ferroelectric powders were ground in a ball-mill in order to reduce particle sizes and then mixed together with a frit and an organic vehicle, such as terpineol and ethyl cellulose, and phosphate ester according to the paste formulas. Then, the paste was transferred on stainless steel substrates by screen printing technique. The thick films were dried and fired in an electric oven and a muffle kiln, respectively. Finally, they were characterized for phases and crystal structures, microstructures, and electrical properties. The experimental details are described in this chapter.

3.1 Pb-based ferroelectric powder comminution

Pb-based ferroelectric powders used in this research are ACL 4040, ACL 4050, and ACL 4055 (Advanced Ceramics Limited, U.K.). ACL 4040 is a hard piezoceramic formulation for high power device applications. On the other hand, ACL 4050 and ACL 4055 are soft piezoceramic formulations for transformer applications. Each of them was put in a laboratory ball mill, together with distilled water and zirconia balls (5.0 mm in diameter) as milling media and then milled for 18 hours (210 rpm in speed). The similar method was applied for 72 hour milling but with 3.0 mm in diameter balls and at 285 rpm. The slurries were dried at 100°C in an electric oven, following by milling of dried powders using alumina mortar to eliminate large powder lumps and then passed through a sieve (40 mesh).

3.2 Pb-based ferroelectric powder characterization

Pb-based ferroelectric powders were examined for the particle size and the particle size distribution (PSD) by mastersizer (MALVERN Instruments: Mastersizer-S). The particle size ranges from 0.05 μm to 900 μm can be measured. He-Ni Laser generated the light for using in this machine. Distilled water and NaHMP powder were used as the dispersing medium and additive, respectively. NaHMP solution was prepared from 1 g NaHMP powder per 1 litre distilled water. It was mixed with Pb-based ferroelectric powder and put in an ultrasonic bath before measuring the particle size and the particle size distribution.

3.3 Pb-based ferroelectric paste

3.3.1 Materials

Materials using in ferroelectric paste formulas are shown in Table 3.1.

3.3.2 Frit preparation

Frit is an important material for sinterability. The lower-melting frit forms liquid phase to promote densification in the Pb-based ferroelectric thick film during sintering. The firing temperature of Pb-based ferroelectric thick film can be lowered by mixing with frit. In this study, the starting materials for frit which are commercially available were PbO ($\geq$ 99% purity, Fluka Chemika), B_2O_3 ($\geq$ 97% purity, Fluka Chemika), and Bi_2O_3 (Carlo Erba) powders. The frit preparation procedure is given in Fig. 3.1.

Table 3.1 Materials using in ferroelectric paste formulas

Materials	Sources
ACL 4040 (hard piezoceramic)	Advanced Ceramics Limited (U.K.)
ACL 4050 (soft piezoceramic)	Advanced Ceramics Limited (U.K.)
ACL 4055 (soft piezoceramic)	Advanced Ceramics Limited (U.K.)
Terpineol	Fluka Chemika (Switzerland)
Ethyl cellulose	Fluka BioChemika (Switzerland)
Triton QS-44 solution (Phosphate ester)	Sigma Chemical Co. (U.S.A.)
Lead (II) oxide yellow (PbO)	Fluka Chemika (Switzerland)
Boric anhydride (B_2O_3)	Fluka Chemika (Switzerland)
Bismuto tri-Ossido (Bismuth Trioxide, Bi_2O_3)	Carlo Erba

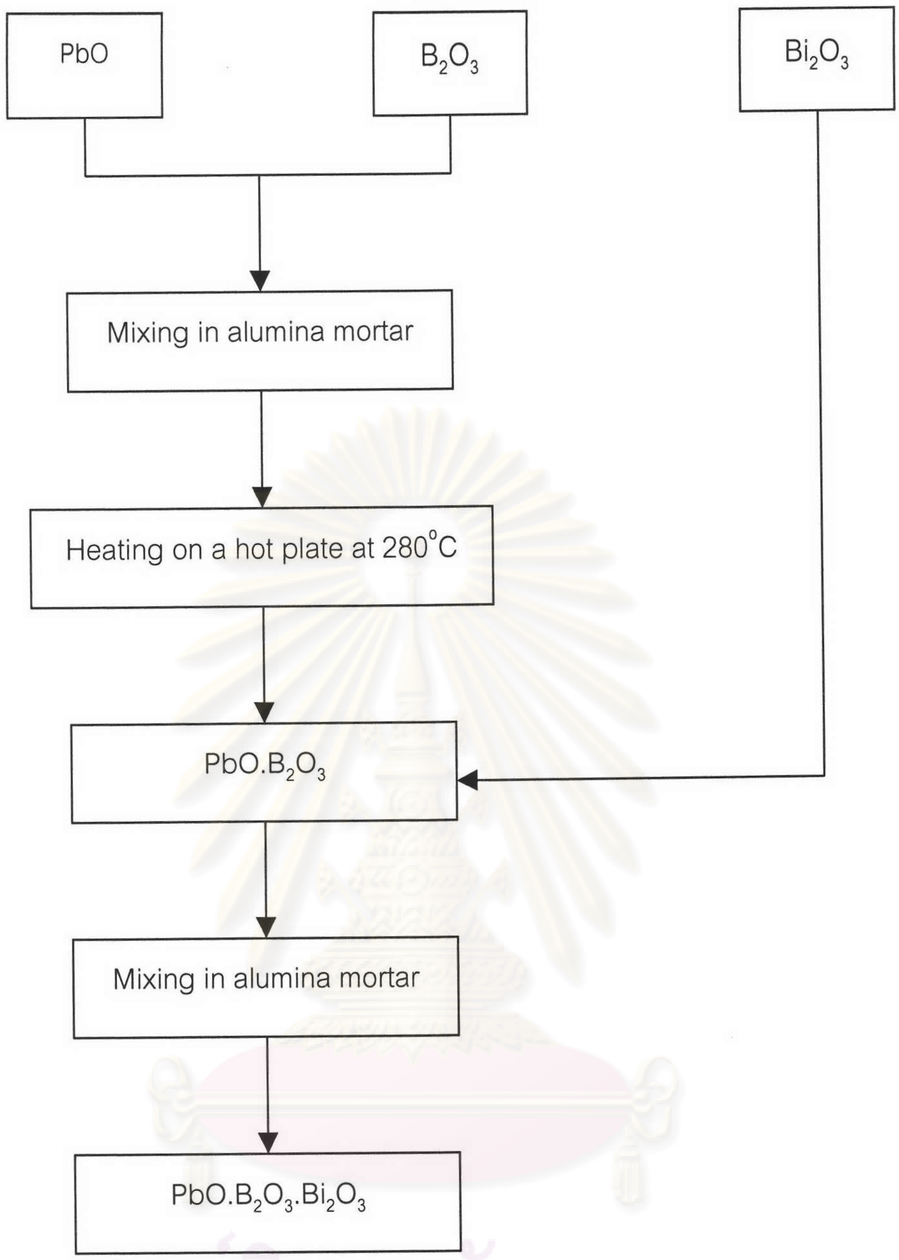

Fig. 3.1 Flow diagram of frit preparation for ferroelectric paste formulas

3.3.3 Organic vehicle preparation

An organic vehicle is generally composed of solvent and binder. In this research, terpineol was used as a solvent and ethyl cellulose as a binder for preparing the organic vehicle. They were mixed together before using in paste formulas. The procedure of its preparation is shown in Fig. 3.2.

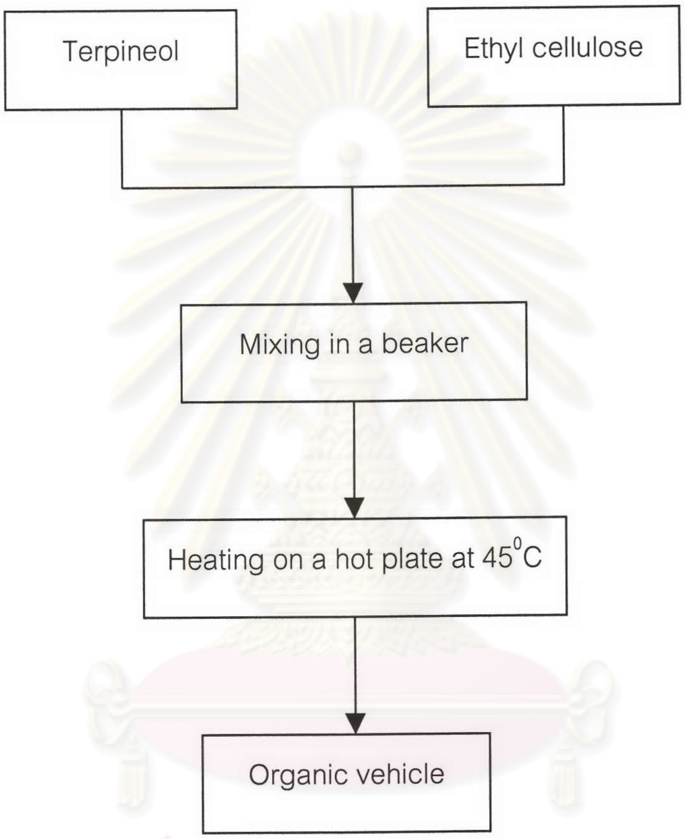

Fig. 3.2 Flow diagram of organic vehicle preparation

3.3.4 Ferroelectric paste preparation

Pb-based ferroelectric paste formulas consisted of ferroelectric powder, terpineol, ethyl cellulose, phosphate ester, and frit varying amount of them depend on each formula. The flow chart of Pb-based ferroelectric paste preparation is given in Fig. 3.3. These starting materials were mixed together, and then they were stirred with a paste-stirring machine as shown in Fig. 3.4 to increase homogeneity for 40 minutes. After that, the ferroelectric paste was screen-printed onto stainless steel substrates.

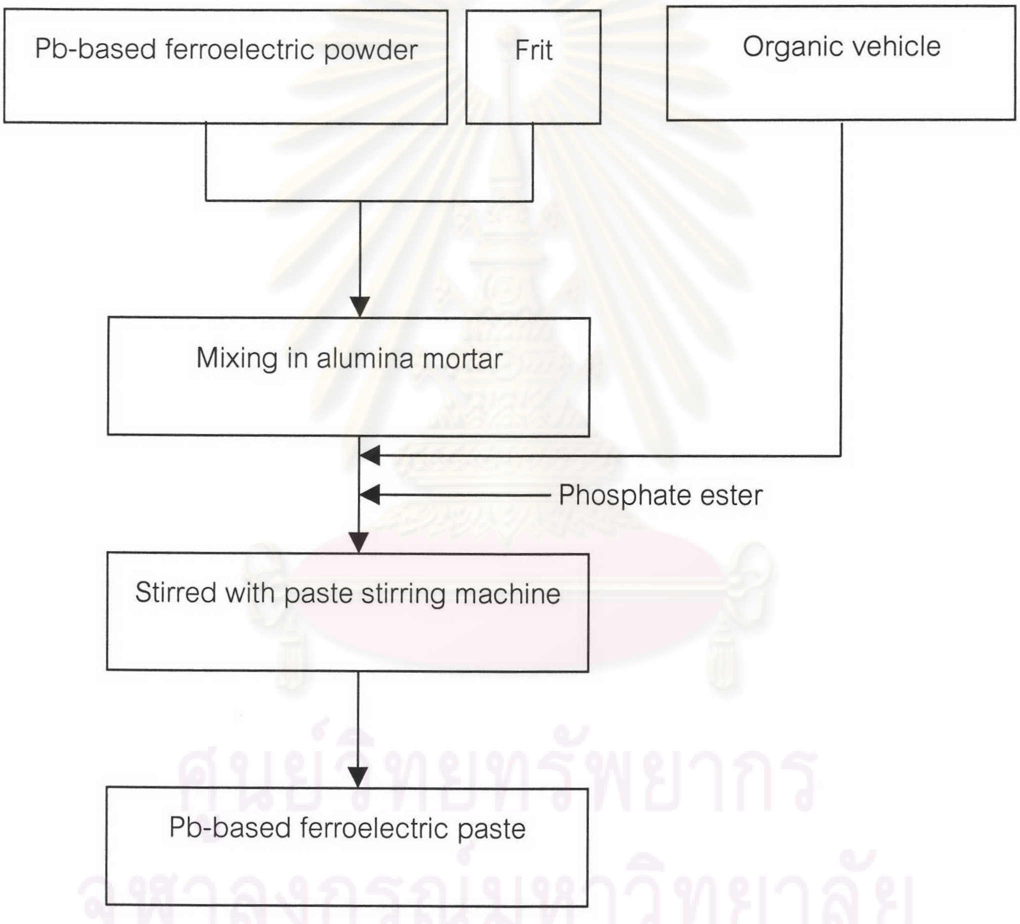

Fig. 3.3 Flow diagram of Pb-based ferroelectric paste preparation

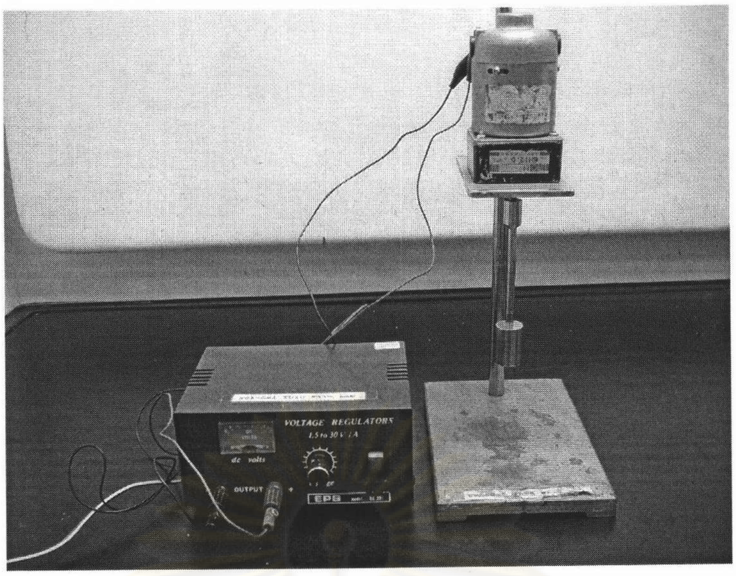

Fig.3.4 The home-made instrument for the paste-stirring machine

3.4 Ferroelectric thick film preparation by screen printing

Pb-based ferroelectric paste was screen-printed onto stainless steel substrates by manually screen printing. The screen printing equipments are shown in Fig. 3.5. The mask screen size of 5 × 5 mm^2 was made for a pattern of ferroelectric thick films. The attack angle was about 45° during manually screen printing. The ferroelectric thick films on stainless steel substrates were placed at a room temperature until they were dried.

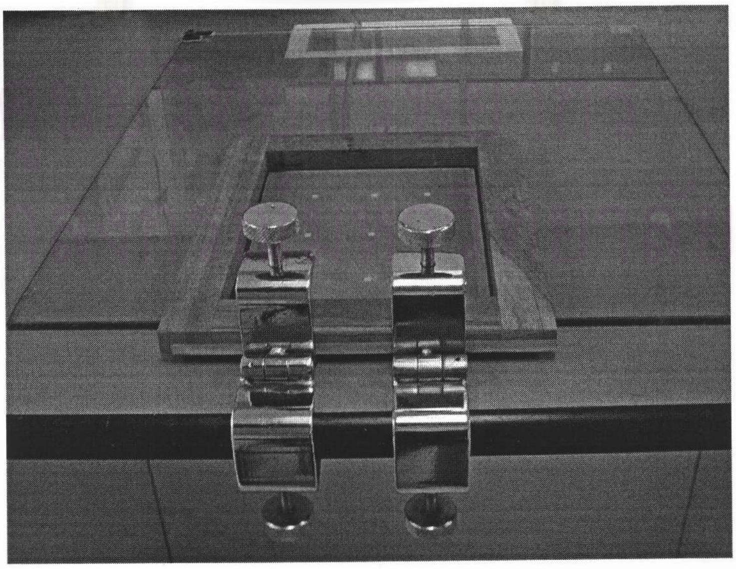

Fig. 3.5 The screen printing equipment

3.5 Drying and firing condition

The Pb-based ferroelectric thick films on stainless steel substrates were dried in an electric oven at 100°C for 2 hours. After that, they were put in a closed-alumina crucible and fired in a muffle kiln at 680°C, 750°C, 800°C, and 850°C for 1 hour to determine the optimum temperature. Firing condition is given in Fig. 3.6.

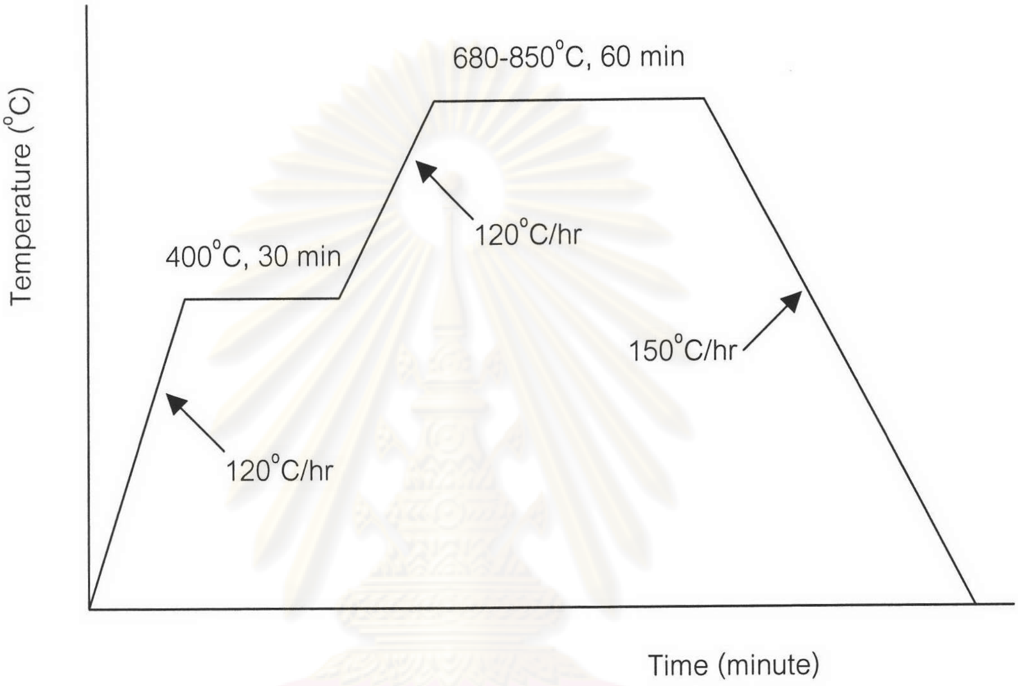

Fig. 3.6 Firing condition for Pb-based ferroelectric thick films

3.6 Pb-based ferroelectric thick film characterization

3.6.1 Phase characterization

The crystal structures and phases of stainless steel substrates, Pb-based ferroelectric powders, and Pb-based ferroelectric thick films were examined by the x-ray diffractometer (CuKα; JEOL: JDX-3530). The machine was calibrated using high purity silicon as an external reference standard before measurement.The stainless steel substrates were scanned using 2θ range of 20-90° with 0.04 degree for step angle and 1 second/step for count time. The similar condition was used for Pb-based ferroelectric powders and Pb-based ferroelectric thick films but the step angle was changed from

0.04 to 0.02 degree because more details of phases and crystal structures could be detected.

3.6.2 Microstructure characterization

The surfaces of Pb-based ferroelecric thick films were observed both before firing and after firing by reflected light microscope (ZEISS: Axiotech 100HD). The defects at the surfaces, for example, crack, pinhole, and pore were examined and detected by this microscope. Then, the samples after firing were coated with gold for 80 seconds by a sputtering (JEOL: JFC-1200). The specimens were then investigated for surface microstructure by scanning electron microscope (JEOL: JSM-6301F) for X500, X5,000, and X20,000 magnifications.

In addition to characterization of the surface, the cross-sectioned of the ferroelectric thick films were also examined for an interfacial layer between the film and the substrate. The specimens were coated with carbon at 7.5 volt and 30 A by a sputtering (SPI Supplies: SPI-MODULE), and then they were characterized by the scanning electron microscope.

3.6.3 Electrical measurement

3.6.3.1 Thickness measurement

The fired Pb-based ferroelectric thick films were mounted in a resin and a hardener. The samples were cross-sectioned by a diamond saw and were ground by SiC papers until the surfaces were smooth. After that, they were polished with a diamond powder until quite smooth and then they were measured for the film thickness at a magnification of X200 using the reflected light microscope (ZEISS: Axiotech 100HD). The finished specimen for thickness measurement is shown in Fig. 3.7.

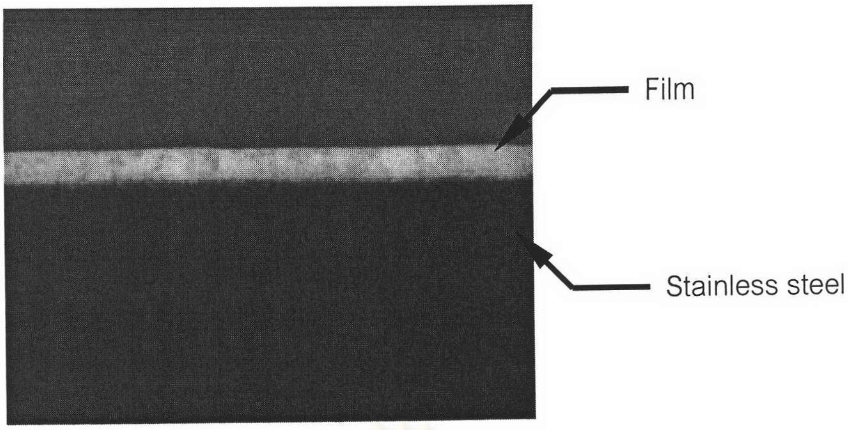

Fig. 3.7 The specimen for thickness measurement

3.6.3.2 Dielectic constant and dissipation factor measurement

In this research, dielectric constant (K) and dissipation factor (tanδ) of the thick film were measured at room temperature using an impedance analyzer (Hewlett Packard: HP4194A). Pb-based ferroelectric thick films were Au-sputtered for 120 and 150 seconds to get top electrodes and Cu plate was used for a bottom electrode during measurement. The capacitance and dissipation factors were measured at four different frequencies, including 1 kHz, 10 kHz, 100 kHz, and 1 MHz by this machine. The measured capacitance was used to calculate the dielectric constant. The dielectric constant was calculated using the equation:

$$\boxed{K=C_o t/\varepsilon_o A}$$

Where C_o is the capacitance (F)

t is the thickness of the thick film after firing (m)

ε_o is the permittivity of free space (8.854×10^{-12} F/m)

A is the electrode area (0.282×10^{-6} m^2)

3.6.4 Surface roughness

The surface roughness of Pb-based ferroelectric thick film was measured by a surface profile measurement instrument (Hills & Valleys: Dektak^3 ST). It is an advanced surface texture measuring system, which accurately measures surface texture below sub-micron and film thickness upto 131 microns. A stylus is made of diamond and it has 2.5 μm in radius. A scan length was 500 μm in this measurement.