Chapter 3

Experimentals

1. Materials

1.1. Samples : 1-3 composite PZT/epoxy, 0-3 composite PZT/P(VDF-TrFE), PZT, lithium niobate ($LiNbO_3$), lithium tantalate ($LiTaO_3$)

1.2. Silicone oil (Fluka 85415)

1.3. Air drying silver conductive paint (SPI 5002)

1.4. Gold wire

1.5. Solder

1.6. Grinding paper (Buehler)

1.7. Thermally conductive adhesive (RS 850-984)

1.8. Hardener (Araldite HY 5138)

2. Equipments

2.1 Furnace (Thermolyne 46100, Memmert : ULF-400)

2.2 Compressor (Carver : 2699)

2.3 Automatic dicing saw (Disco : DAD321)

2.4 Glass petri dish

2.5 Hotplate (PNP HS-2)

2.6 Kilovolt power supply(PASCO scientific SF-9586)

2.7 He-Ne laser (Uniphase 1135P)

2.8 Diode laser (Lisa HL25)

2.9 Beam spliter

2.10 Reference mirror and piezoelectric transducer

2.11 Photodiode detector(BPX 65)

2.12 Translation stage (Newport 460A)

2.13 Rotary stage (Newport 481A)

2.14 Feedback circuit
2.15 Oscilloscope (HAMEG HM604)
2.16 Lock-in amplifier (Princeton 5210, Stanford Research Systems SR530)
2.17 Function generator (Stanford Research Systems DS 340)
2.18 Peltier element (DT12-6)
2.19 Temperature sensor (Pt100)
2.20 Electrometer (Takeda Riken 8651))
2.21 Vacuum pump(Welch Directorr 8915)
2.22 Multimeter (Fluke 8840A)
2.23 Multimeter (Digicon BM-870A)
2.24 Brass chamber
2.25 Aluminum plate
2.26 Resistance (Rheostat 11 ohms. 6.2 Amps.)
2.27 Built-in modulated Laser (Lisa)
2.28 Power supply (0-30 V, 0-12 V, 0-30V, 1-3 A)
2.29 Scanning electron microscope (JEOL JSM-5200)
2.30 Differential scanning calorimeter (Perkin Elmer DSC7)
2.31 Vacuum coating system (JEOL JEEE-400)

3. Experimental Procedures

The experiments in present work were separated into 2 parts in which mainly focus on the properties of the composite.

3.1 Sample Preparation

The samples used in the present work were composited in two connectivities. The first connectivity was 1-3 composites PZT/epoxy, and the second was 0-3 composites PZT/P(VDF-TrFE). The samples used in this work were prepared at Smart Material Research Center, Applied Physic Department, Hong Kong Polytechnic University, Republic of China.

3.1.1) 1-3 composite PZT/epoxy preparation

1-3 composites PZT/epoxy were fabricated from PZT disk and Araldite LY5138-2/HY5138 epoxy using dice-and-fill techniques. The PZT powders (PKI 502) were shaped into 10.5 mm diameter disks with thickness of 1.5 mm. The disks were sintered at temperature shown in Figure 3.1. After that the disks were annealed at temperature shown in Figure 3.2.

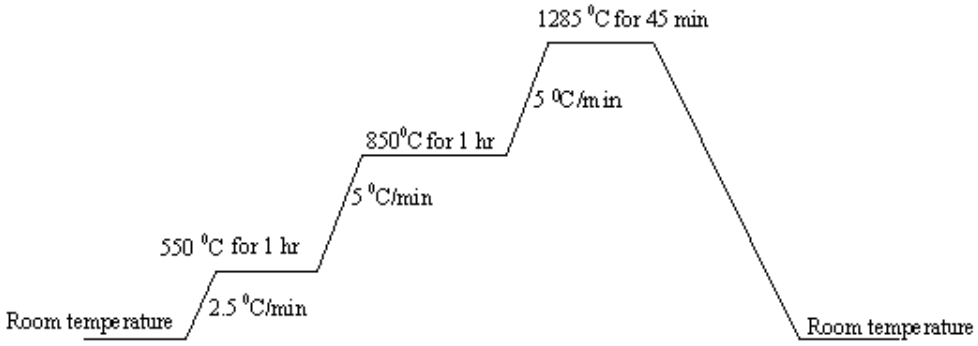


Figure 3.1 Heating rate used in the sintering process

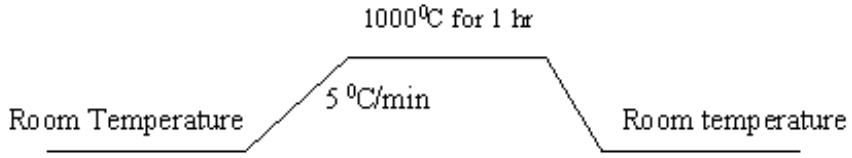


Figure 3.2 Heating rate used in annealing process

In order to cut the disks with dicing machine, each ceramics disk was placed on a glass petri dish and put in the dicing machine (Figure 3.3). Parallel cuts were made in the disks. A total of 10 ceramic disks were diced, five were diced with a saw blade of 200 μm thickness, and another five disks were diced using a blade of 80 μm thickness. After cutting, Araldite LY5138-2/HY5138 (100: 23) epoxy was poured over the disks. Thereafter the disks were placed in the low-pressure chamber for 15-20 minutes in order that the epoxy could fill in the grooves and the bubbles trapped in the grooves were removed. The low-pressure chamber is shown in Figure 3.4. The

pressure in chamber were around 1.3×10^{-1} Pa. After that the samples were left at 50-60 ^{0}C for half an hour, allowing the epoxy to cure.

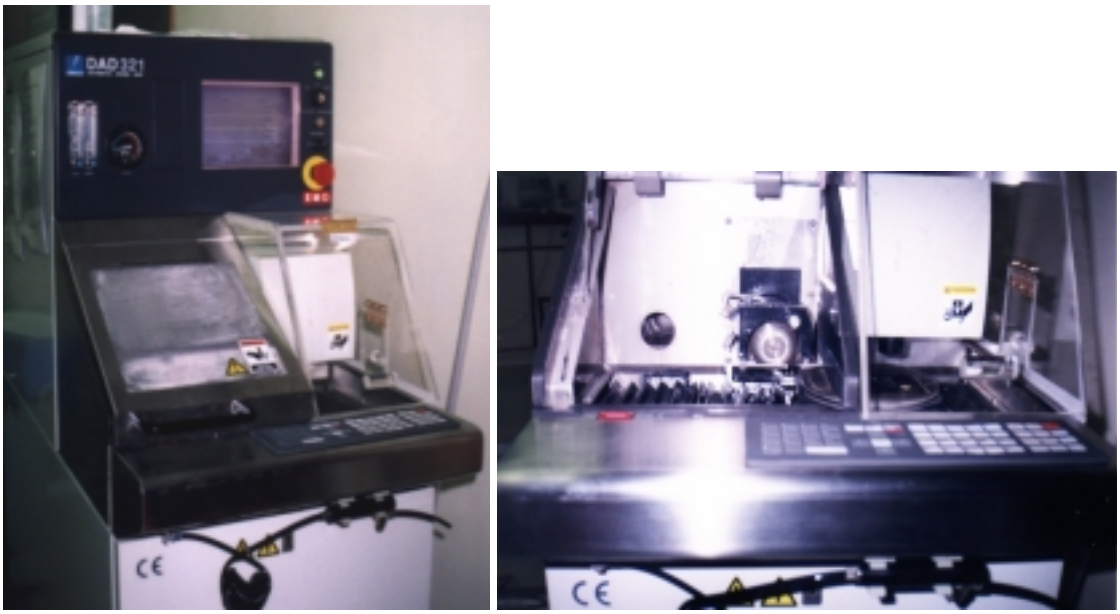


Figure 3.3 Dicing machine

Figure 3.4 Low-pressure chamber

The second parallel cuts were made normal to the first and the process of filling the epoxy was repeated (Figure 3.5).

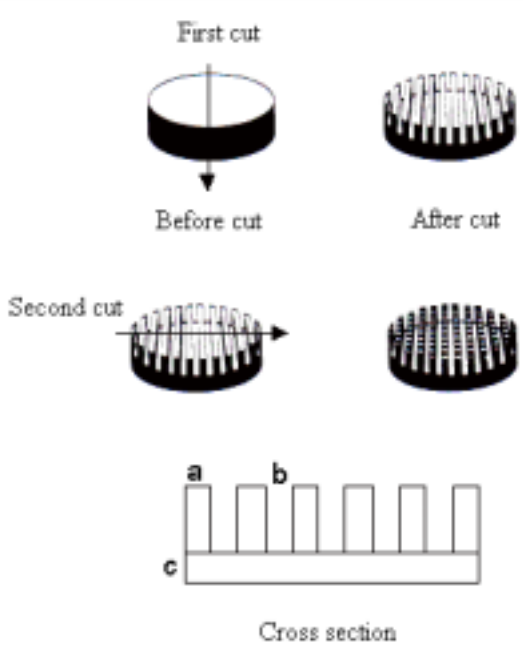


Figure 3.5 Dicing direction

The volume fraction of ceramic were calculated by

$$volume\ fraction\ of\ \ ceramic = \frac{a^2}{(a+b)^2} \tag{3.1}$$

Ceramic content in the epoxy was varied as shown in Table 3.1. Final finishing of the composite to the desired thickness was done by lapping, using abrasive papers of various grades.

Table 3.1 Ceramic and epoxy parameters used in the composite fabrication

Volume fraction of ceramic(ϕ)	Ceramic width(mm)	Epoxy width(mm)
0.4	0.325	0.21
0.6	0.325	0.08
1	-	-

3.1.2) 0-3 composite PZT/P (VDF-TrFE)

0-3 composite PZT/P (VDF-TrFE) were fabricated by mixing the copolymer and PZT powder. The P(VDF-TrFE) 70/30-mol% copolymer used in the present work was supplied by Piezotech. The PZT powders PKI 502 (Ultra-sonic Powders Ltd.) were annealed and sintered at temperature shown in Figures 3.6 and 3.7, respectively

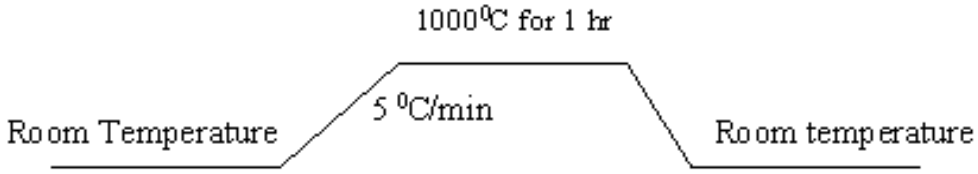


Figure 3.6 Heating rate used in the annealing process

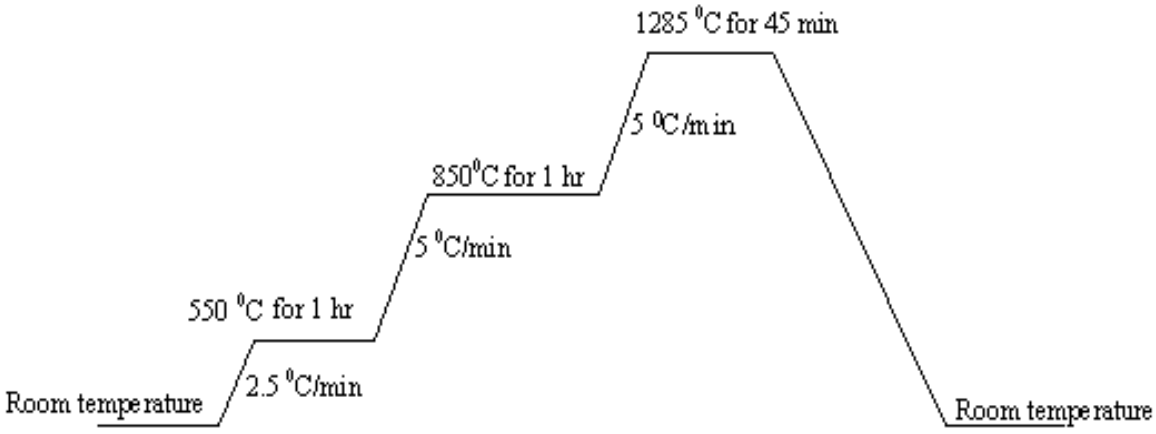


Figure 3.7 Heating rate used in the sintering process

The PZT powders were crushed by hand milling. The mean particle size is about 1 μm. Suitable amounts of the copolymer and PZT powders in the mixture was calculated by

$$m^c = m^p \times \frac{\rho^c}{\rho^p} \times \frac{\phi}{1-\phi} \tag{3.2}$$

m^c	=	Mass of PZT powders	
m^p	=	Mass of copolymer	= 1 g
ρ^c	=	Density of ceramic	= 7.7
ρ^p	=	Density of copolymer	= 1.9
ϕ	=	Volume fraction of ceramic	= 0.3

$$m_c = 1 \times \frac{7.7}{1.9} \times \frac{0.3}{0.7} = 1.737\ g$$

One gram of the copolymer pellet was dissolved in methyl-ethyl-ketone (MEK) 20 ml. And 1.737 grams of PZT powders were blended into the P(VDF-TrFE) solution to form composites with 0.3 volume fraction of ceramic. The mixture was stirred by magnetic stirrer, slowly warmed until it became viscous and agitated in an ultrasonic bath for one hour to ensure that the ceramic powder was distributed evenly in the copolymer solution. In order to evaporate the solvent (MEK), the composites were left at 85 ^{0}C for a day. After evaporation of the solvent, the composites were compressed into disk sample by the following process:

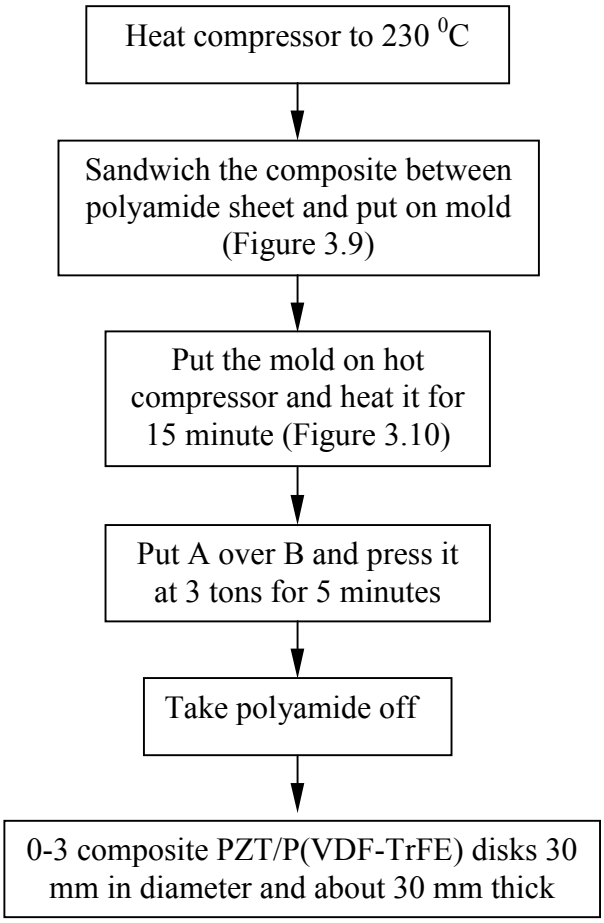


Figure 3.8 The compression process

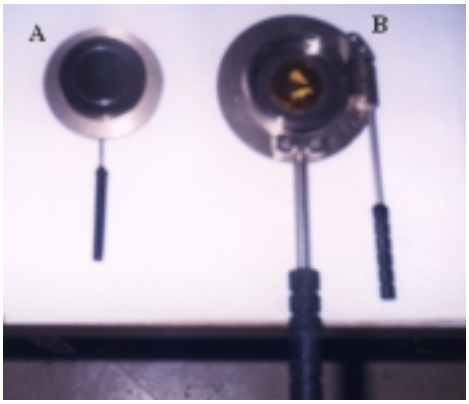


Figure 3.9 The composites that were sandwiched between polyamide sheet were put on mold

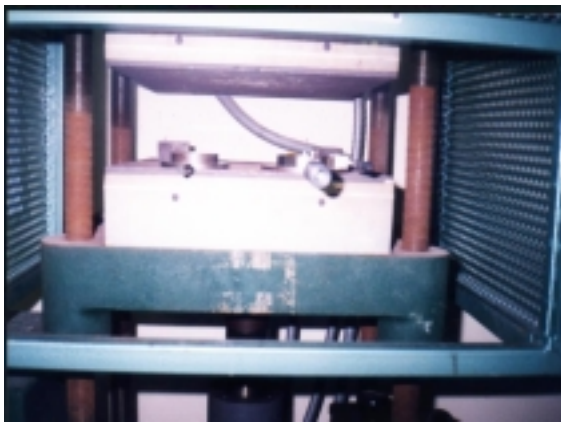


Figure 3.10 The mold was heated by hot compressor.

Samples of the 1-3 PZT/epoxy and the 0-3 PZT/P(VDF-TrFE) composites are shown in Figure 3.11.

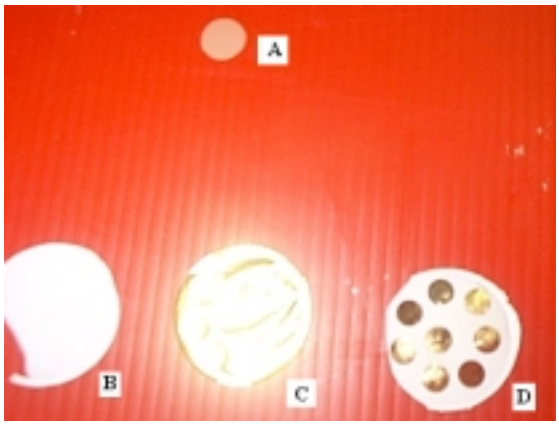


Figure 3.11 Photograph of A) 1-3 composite PZT/epoxy B) 0-3 composite PZT/PVDF-TrFE) C,D) 0-3 composite PZT/P(VDF-TrFE) with gold electrode

3.1.3) Poling

The poling of the piezocomposite which is an active phase of the 1-3 composite is an important stage in the study of the pyroelectric and piezoelectric effects. This can be explained that the adjoining dipoles form regions of local alignment called “domains”. Each alignment gives a net dipole moment to the domain, leading to a net polarization in the sample. The direction of the polarization among neighboring domains is random, however, so the ceramic element has no overall polarization (Figure 3.12a). The domains in a ceramic element are aligned by exposing the element to a strong direct current electric field, usually at a temperature slightly below the Curie point (Figure 3.12b). Through this polarizing *(poling)* treatment, domains most nearly aligned with the electric field expand at the expense of domains that are not aligned with the field, and the element lengthens in the direction of the field. When the electric field is removed most of the dipoles are locked into a configuration of near alignment (Figure3.12c). The element now has a permanent polarization, the remanent polarization, and is permanently elongated.

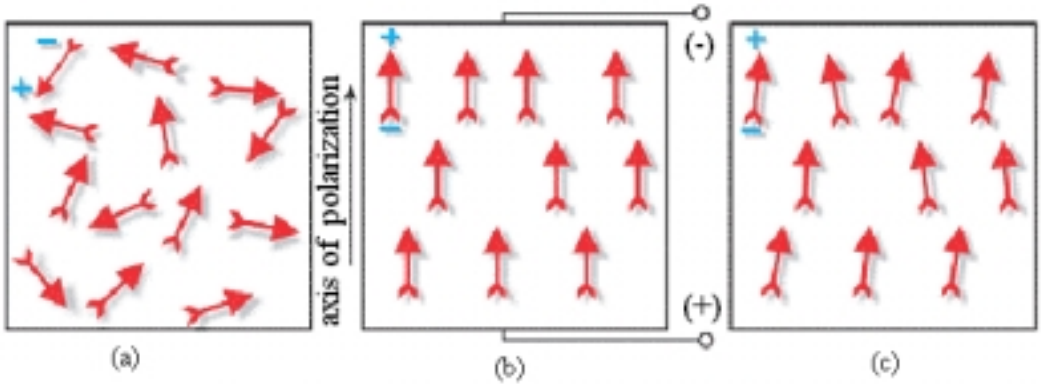


Figure 3.12 Polarizing (Poling) a piezoelectric ceramic (a) random orientation of polar domain prior to polarization (b) polarization in DC electric field (c) remanent polarization after electric field removed.

Because the epoxy has no spontaneous polarization, only PZT rods in the 1-3 composite PZT/epoxy can be polarized under high field. The sample is put in silicone oil (Figure 3.13) to avoid spark of high electric field during poling process. In order to

align dipole in the PZT rods, the electric field of 10 kV/mm is applied to the composite for 15 minutes.

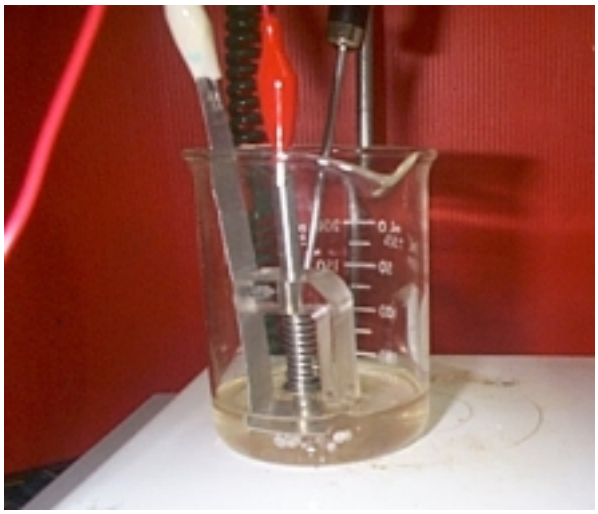


Figure 3.13 Poling setup

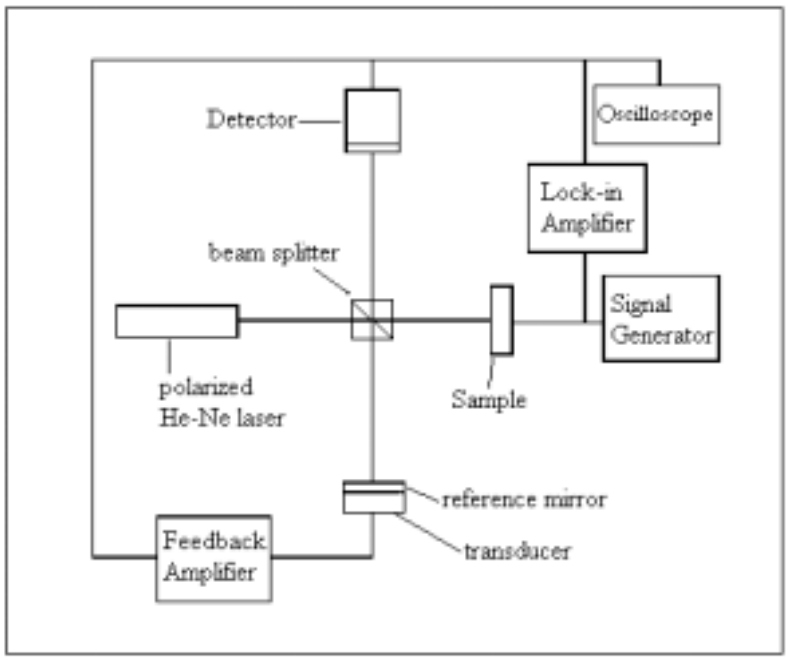
The poling procedure of the 0-3 composite PZT/P(VDF-TrFE) is as follows:

"Samples are heated to 120 ^{0}C (above Curie temperature of P(VDF-TrFE)) and an electric field of 30 kV/mm is applied to the composite for an hour. When the electric field is applied to the sample (while the copolymer is still paraelectric), only the PZT phase is poled. After that the sample is cooled to 60 ^{0}C and an electric field of 40 kV/mm is applied to the sample in order to pole the copolymer phase in the same direction as ceramic phase."

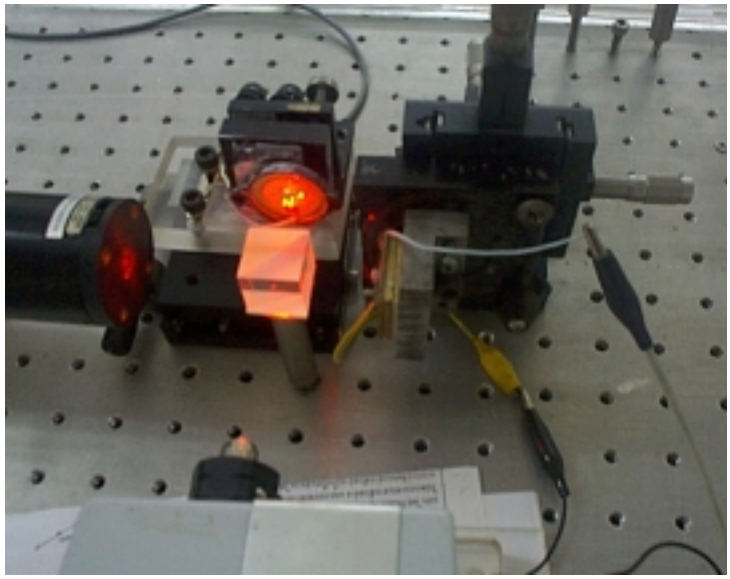
3.2 Characterization

3.2.1) Piezoelectric measurements

A single beam interferometer used in the present work is shown schematically in Figure 3.14. The laser used is a 10 mW He-Ne laser (λ=632.8 nm). The laser beam is split into two half-power beams; a probe and a reference beam. The probe beam is reflected from the sample, whose surface is made reflective by a small piece of mirror (Figure 3.15). The reference beam is reflected from the reference mirror mounted on the piezoelectric transducer connected to the feedback loop. This loop stabilize the system at a point where the path difference is $\lambda/4$, where the change in light intensity is maximized for small change in the displacement Δd of the sample surface. After bouncing back from the sample surface and the reference mirror, the probing beam and the reference beam are recombined by the same beam splitter and formed the interference pattern. When an AC field is applied to the sample, small sinusoid displacements are obtained, giving the interference intensity changes at the point of detection. This optical signal is converted to the voltage change by photodiode. This voltage is detected by a lock-in amplifier as V_{out}, an rms value. Knowing V_{out} and driving voltage, the magnitude of the piezoelectric coefficient can be calculated using equation (2.44).



(A)



(B)

Figure 3.14 (A) Schematic of the interferometer adapted to measure piezoelectric coefficient. (B) The photograph of interferometer used in the present work.

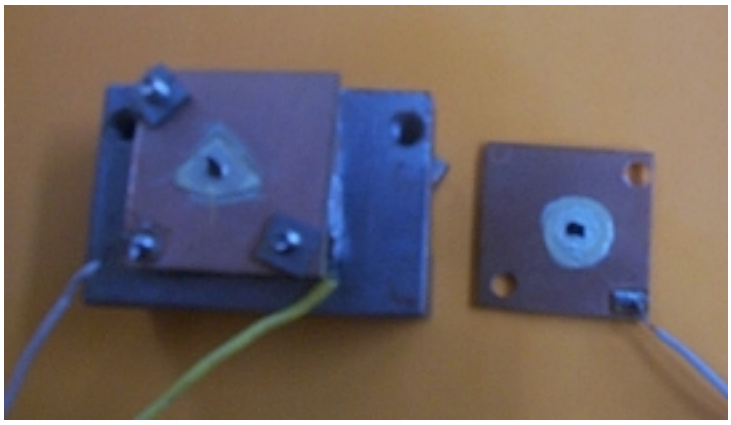


Figure 3.15 The sample, whose surface was made reflective using a small piece of mirror attached onto the sample.

The experimental procedure was as follows:

A] Turned on the laser, the detector and the oscilloscope.

B] Slightly adjusted both the reference mirror and the sample holder so that the central fringe of the interference pattern achieved at the detector.

C] Turned on the feedback circuit to calibrate mode.

D] Observed the interference fringe shifts on the oscilloscope and recorded the peak-to-peak voltage of interference pattern as $V_{p\text{-}p.}$

E] Applied AC electric field (from function generator 1 kHz, 1-10V) across the sample. Turn the feedback circuit to feedback mode to measure the amplitude of the sample vibration.

F] Recorded the magnitude and phase of the output voltage from lock-in amplifier connected to detector.

G] Calculated the displacement of sample surface(d_{ac}) using equation(2.44).

H] Plotted the variation of the sample surface displacement with the apply voltage. The slope is the piezoelectric coefficient in thickness mode(d_{33}).

I] Repeated D) to H) in the frequency range of 2 kHz to 10 kHz.

3.1.2) Pyroelectric measurements

The pyroelectric coefficients of the 1-3 composite PZT/epoxy were measured using the direct method. In this method, the sample was heated or cooled at a controlled rate and the resulting pyroelectric current was measured. The method gives the pyroelectric coefficient directly, without the need to infer temperature changes from energy absorption.

Figure 3.16 shows the arrangement used for pyroelectric measurement. The measurements were performed under low pressure condition (around 10^{-3} Pa) in order to minimize the humidity from surrounding environment. The sample was mounted in a small chamber. The sample temperature was controlled by means of peltier elements (DL12-6), sandwiched between 2 aluminum plates, whose dimensions matched with the peltier element surface. The heating and cooling rate were controlled by the magnitude and direction of the current passing through the peltier element.

The temperature of the sample was measured using a calibrated Pt-100 resistance thermometer and converted into an equivalent voltage by means of a linearised RTD module. In order to ensure that it was accurately monitoring the temperature of the sample. It was necessary to vary the temperature slowly, allowing the temperature to uniformly distribute in the sample.

Figure 3.17 shows the dimension of the temperature sensor (Pt100), which was used in this work. The DC electric field applied across the temperature sensor series with a resistance of 12 kΩas shown in Figure 3.18. The charge changing upon heating and cooling was measured by electrometer. Variations of polarization with temperature of samples were plotted. According to equation (2.47), the slope of the plot is the pyroelectric coefficient.

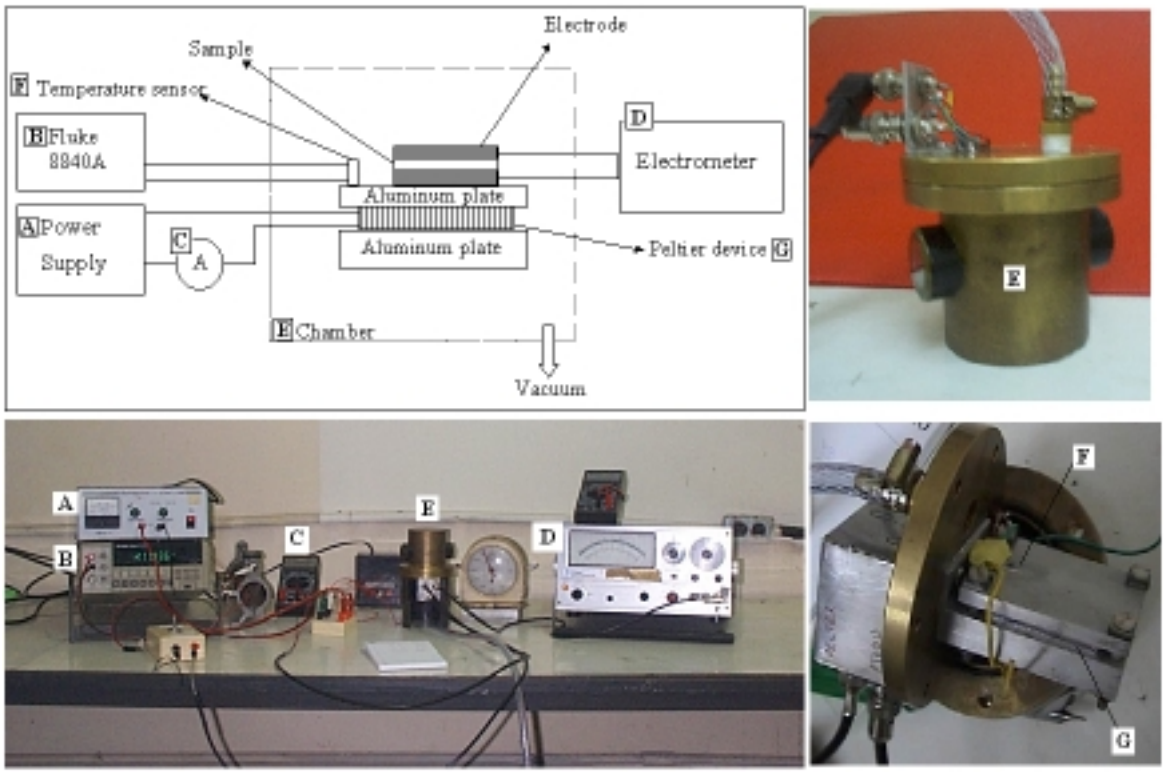


Figure 3.16 The experimental arrangement used to measure the pyroelectric coefficient.

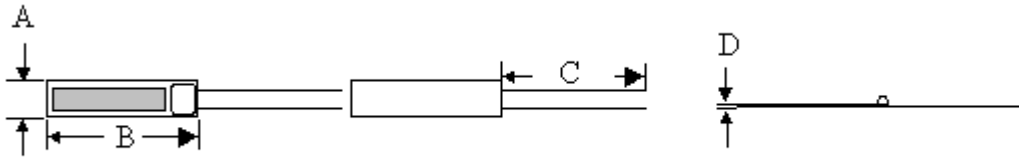


Figure 3.17 Temperature sensor A×B×C×D as 2×5×11×1.1 mm.

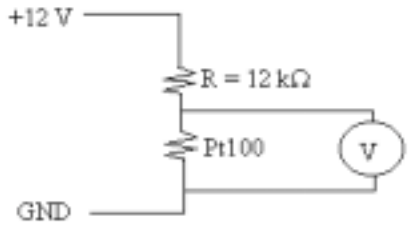


Figure 3.18 The temperature sensor circuit

The temperature sensor (Pt100) resistance is 100 Ω at 0 ^{0}C and its resistance change 0.385 Ω when its temperature change 1^{0}C. The temperature can be calculated by

$$R_{total} \approx 12k\Omega$$

$$I_{total} = \frac{V_{total}}{R_{total}}$$

$$= \frac{12\text{Volt}}{12\text{k}\Omega}$$

$$= 1 \text{ mA}$$

$$\text{V}_{\text{measured}}(mV) = 1(100 + 0.385t) \qquad (3.3)$$

The experimental procedure was as followed:

a] Warmed the electrometer for an hour

b] Put the sample attached to the aluminum plate on the sample holder

c] Turned on the vacuum pump.

d] Applied the DC electric field of 1 Amp through the peltier elements in order to heat the sample and wait for 5 minutes.

e] Detected the voltage across the temperature sensor from multimeter and the charge of sample from the electrometer.

f] Applied the DC electric field of -1 Amp through the peltier elements in order to cool the sample and wait for 5 minutes.

g] Detected the voltage across the temperature sensor from multimeter and the charge of sample from the electrometer

h] Repeated d] to g] for several times.

i] Calculate the polarization of the sample from

$$P = \frac{\Delta Q}{A} \qquad (3.4)$$

where P is the polarization of the sample , ΔQ is the change of total charge due to a change in sample temperature and A is the electrode area.

j] Calculate the temperature from equation (3.3)

k] Plotted the variation of the polarization of the sample with temperature.

3.1.3) Thermal diffusivity measurements

The thermal diffusivity of the samples was measured using the technique based on the measurement of the phase retardation of the thermal wave passing through the sample. Figure 3.19 shows the sample mounting.

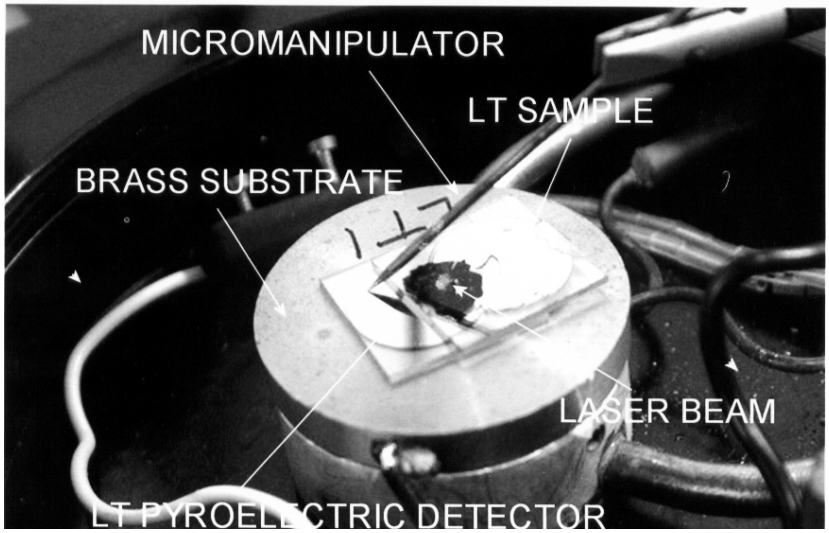


Figure 3.19 The photograph of the sample holder in thermal diffusivity measurement

The detectors were lithium tantalate with gold electrode. The experimental procedure is as follows:

A] Painted the black color onto the front surface of the test sample to improve the laser beam absorption.

B] Painted a thin layer of the contact cement onto front surface of detector and the back surface of sample.

C] Pressed the cemented surfaces together.

D] Connected the detector to a brass plate that acts as a substrate.

E] Used 5 V_{rms} and 1 Hz of a function generator to drive and modulate the laser beam.

F] Projected the sinusoidally modulated in intensity laser beam in the front of the sample surface.

G] Detected the pyroelectric current and phase lag from lock-in amplifier.

H] Repeated E] to G] for 10-15 different modulation frequencies in range 1-10 Hz

I] Analyzed the data by means of Mathematica program.