CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Materials and Fabrication

In this experimental, piezoelectric ceramic particles are incorporated into the cement based composited using normal mixing, pressing and curing method. The synthesis and processing, composition, structure, properties and relative relationship are studied experimentally by using measuring instrument as X-ray diffractometry, LCR-meter, d_{33} meter, Sawyer-Tower circuit, SEM and PFM.

3.1.1 Piezoelectric ceramics fabrication

Powder fabrication

In this work, all powder compositions have been prepared by a solid-state mixed oxide technique. All commercially available starting compounds which were used for the preparation of the compositions in this study are listed in Table 3.1, along with the supplies, formula weights and purities.

The mixing process schematically illustrated in Fig. 3.1 was employed as a routine processing procedure for powder preparation. In the mixing process, the calculated relevant proportions of constituents were weighed, suspended in ethanol and intimately mixed in a ball-mill with zirconia media. Drying was carried out for 2 h (the sample dish was placed on a hotplate with the magnetic stirring in action to prevent gravitational separation of the components). The dried powder was then ground and calcined in closed alumina crucibles.

| Powders | Source | Formula weight | Purity (%) |
|------------------|-----------------|----------------|------------|
| РЬО | Fluka* | 223.189 | 99.99 |
| ZrO ₂ | Riedel deHaen** | 123.22 | 99.00 |
| TiO ₂ | Riedel deHaen** | 79.898 | 99.99 |

 Table 3.1 Specifications of the starting materials used in this study

Note: * Fluka Chemical GmbH, Switzerland

** Riedel deHaen Laborchemikalin GmbH&Co. KG, France

Ceramic fabrication

All ceramic fabrication was carried out by adding 3 wt% polyvinyl alcohol (PVA) binder, prior to pressing as pellets in a uniaxial die press at 100 MPa. The sample was placed on the alumina powder–bed inside alumina crucible. In order to reduce loss of volatile components *e.g.* lead, the sample was surrounded with an atmosphere powder of the same composition as the pellet. Alumina crucible was closed with an alumina lid before insertion into a high temperature sintering furnace. After the binder have been burn out at 500 °C for 1 h, sintering was carried out with dwell time of 3 h using heating/cooling rates of 10°C /min at various temperatures between 1200 and 1250 °C, depending on the chemical compositions. The ceramic process schematically also illustrated in Fig. 3.1 Then all ceramic were hammered and sieved size using laboratory test sieve with aperture 150, 300 and 600 Mic. (ASTM-E11).



Fig 3.1 Mixing and calcination processes for powder and ceramic preparation

3.1.2 Lead zirconate titanate, PZT

The modified mixed-oxide method was also developed for preparation of PZT powders. It comprised two mixed oxide reaction stages as follows: in the first stage PbO was reacted with ZrO₂ to give PbZrO₃, and in the second stage, TiO₂ and excess PbO were reacted with the PbZrO₃ to give the final product of perovskite PZT.



Fig 3.2 Two-stage processing route for PZT powders and ceramic

Stage 1) $PbO + ZrO_2 \rightarrow PbZrO_3$;(PZ) (3.1)

Stage 2) $0.52PbZrO_3+0.48TiO_2 + 0.48PbO \rightarrow Pb(Zr_{0.52}Ti_{0.48})O_3$; (PZT) (3.2)

The starting powders of PbO, ZrO_2 and TiO_2 were used, and the mixing process described in 3.1.1 was followed. Conditions for optimizing the calcination for PZ powder and PZT powder at 800°C and 900°C respectively and PZT ceramic were determined sintering at 1200°C. A schematic diagram of the material preparation route for PbZrO₃ and PZT powders and ceramics are illustrated in Fig. 3.2

3.1.3 Composite fabrications

A piezoelectric ceramic (PZT) and cement (ordinary type: ASTM type I cement) were used to prepare cement-based piezoelectric composites. The particle size distributions of piezoelectric ceramic and cement were measured by sieving techniques. Piezoelectric ceramic and Portland cement are mixed together to make cement-based piezoelectric ceramic composites. In order to improving the electrical property, a semiconductor and insulator (carbon graphite and polyvinylidene fluoride) was used as a third phase. Using a normal mixing (missing duration is about 2 min) method, piezoelectric particle and third phase could be incorporated into composites with different ratio of ceramic/cement and ceramic/cement/third phase. The detail can be seen in Table 3.2 and 3.3 respectively. To achieve a uniform mixture, cement and piezoelectric ceramic particle were mix thoroughly first, then carbon graphite powder and polyvinylidene fluoride powder were added into the mixture. The mixing process was continued until the mixture became uniform. Then the mixture was pressed into the model disks (Fig 3.4) to form ceramic–cement composites of 0-3 connectivity.

After axially pressing, the specimens were put in the curing chamber (Fig 3.5) with a temperature of 60 °C and relative humidity of 97% for 72 hours. In order to adding with polyvinylidene fluoride into the ceramic-cement composite, after the mixture were mixed and pressed into the model the sample was then annealed with a temperature of 150 °C for polyvinylidene fluoride to form crystallization. Then, the sample due were put in the curing chamber.

| Siz | Cor | npositio | on of co | mposite | es, <i>x</i> PZ | T-(1-x) | PC | 533 | 0 |
|-----------|----------------------|----------|----------|---------|-----------------|---------|----|-----|-----|
| Matarial | Volume % of <i>x</i> | | | | | | | | |
| Wiaterial | 0 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| РС | 100 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| PZT | 0 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

Table 3.2 Composition of ceramic- cements composites;

Table 3.3 Composition of ceramic- cements composites with third phase adding;

| | Composition of composites, 50PZT-(50-x) PC-x Third phase Volume % of x | | | | |
|-------------|--|------|----|----|----|
| ເສີກຂຶ້ນห | | | | | |
| Material | 0 | 1 | 2 | 5 | 10 |
| РС | 50 | 49 8 | 48 | 45 | 40 |
| PZT Ceramic | 50 | 50 | 50 | 50 | 50 |
| Third phase | 0 | 1 | 2 | 5 | 10 |



Fig 3.3 The model for fabricating cement-based piezoelectric ceramic composites samples



Fig 3.4 The curing chamber

3.1.4 Electrode making

The close adhesion of electrode is important since most piezoelectric have high permittivity and a large fraction of any applied potential will therefore occur across any low permittivity gap between an electrode and the material surface. Electrodes are therefore usually formed by applying a silver or Ag₂O suspension. As considering the thermal properties of cement material, a special silver paint with very low firing temperature is chosen to deal with the composite samples.

3.2 Poling process

In a newly fabrication cement-based piezoelectric ceramic composite, the crystallites, and hence the polar axis, can lie in a large number of directions. This will be cause the material to have only a quasi-isotropic response in its electrical, piezoelectric and other characteristics. A lack of orientation can also exist in certain freshly prepared materials due to there being more than possible orientation for the polar exist and each orientation has two possible directions.

Polar axis orientation is done by a poling technique, which consists of applying a D.C. voltage for a sufficient time to the material. The amplitude and duration of the voltage required for poling very substantially between materials. Some material will pole easily and if used in large-signal switching applications may not even require a preliminary poling cycle. Other can only be poled near their Curie point where the coercive field of the material is small. The maximum poling voltage that can be applied is limited by breakdown and arcing in the material. Hence poling is often done in a silicon oil bath In this experiment, polarizing was carried out in a silicon oil bath with a temperature of 80-160°C. The detail can be seen in Table 3.4. After polarization the specimen were placed in room temperature for 24 hours to maintain the status of polarization.

| System | Poling condition | | | | |
|-------------|-------------------------|----------------------------|----------------------|--|--|
| | Poling field (kV/mm) | Poling temperature (°C) | Poling time (min) | | |
| PC-PZT | 1, 2 | 100, 130, 160 | 30, 45, 60 | | |
| PC-PZT-C | They | 130 | 45 | | |
| PC-PZT-PVDF | 1 | 130 | 45 | | |

Table 3.4 Poling condition of the ceramic-cement composites

3.3 Physical and Microstructure characterization

Structure investigate will explore the micro-structure information, bonding, interface, phase and so on, of the cement-based piezoelectric ceramic composite. And the results will offer the fundamental material characteristic of composite.

3.3.1 X-ray diffractometry

Phase characterization of samples was analyzed X-ray diffraction (XRD) of monochromatic rays. The X-rays are generated by accelerating a beam of electrons onto a pure metal target contained in a vacuum tube. When an X-ray beam enters a crystal, the arrangement of atoms into crystal structures can be inferred from the distribution of intensity in the diffraction pattern. In this work, room temperature XRD (Fig. 3.5) were carried out using the Philips (Model X-pert, Germany) automatic powder diffraction system. The diffractometer was operated at 40 kV with 20 mA current. Monochromatic CuK_{α} radiation of wavelength 1.54 Å was used throughout. Each sample was scanned from 10-60 °.



Fig. 3.5 X-ray diffractometer (Philips Model X-pert)

3.3.2 Scanning electron microscopy, SEM

Scanning electron microscopy (SEM) is a very popular technique used in materials and biological sciences as well as in industry for microstructural analysis at high magnification In the SEM, two of interesting signals are the secondary and backscattered electrons, since these vary according to differences in surface topography as the electron beam sweeps across sample. Other signals may be used to measure different properties, e.g. Auger electrons or characteristic X-ray is normally used to determine chemical composition of sample.

In this work, A JEOL JSM-840A (Fig. 3.6) was used to determine the morphology and interfacial zone of the composites. The specimen was coated with gold for making the electrode. During image acquisition, both backscattered and secondary electron modes were used with an accelerating voltage of 20 kV. Chemical composition of the selected area was quantified by using an energy dispersive X-ray spectrometry (EDX).



Fig 3.6 Scanning electron microscope (SEM, JEOL JSM-840A, Japan)

3.3.3 Piezoresponse Force Microscopy, PFM

Piezoresponse force microscopy (PFM) was customer-built based on the commercial atomic force microscope and used to characterize ferroelectric domains of functional materials. The PFM imaging contrast mechanism, domain configuration and their evolution behavior under the inhomogeneous tip fields in ferroelectric materials.

At present, scanning probe microscopy (SPM)-based techniques provide a powerful tool to imaging and characterizing the static and dynamic properties of ferroelectrics. For the first time, SPM provides a non-destructive, ultrahigh resolution tool to visualize nanoscale domain structures and to evaluate local electromechanical and elastic properties. Currently, the most popular SPM method for imaging ferroelectric domains is piezoresponse force microscopy (PFM), based on detecting the piezoelectric vibration of ferroelectric surfaces induced by the ac field between the probing tip and the sample. Its high spatial resolution, easy implementation, effective manipulation of nanoscale domains and locally quantitative characterization capabilities make it a versatile tool for nanoscale ferroelectric studies. In this chapter we describe the morphology, phase, and interface characterizing ferroelectric domains of bulk ceramic, cement, PVDF and cement-based composites as well. Piezoresponse-mode scanning force microscopy, i.e. piezoresponse force microscopy has become an effective research instrument for characterization of domain structures and physical properties on nanoscale [89, 90]

Based on converse piezoelectric effects of specimens, imaging of piezoresponse-mode SFM is obtained by means of detecting local vibration of piezoelectrics under applied ac voltage. Fig. 3.7 shows the schematic of PFM that is built up on the basis of commercial AFM. Its working mechanism includes the following processes: the PFM probe scans specimen surface in a contact mode, and Ac voltage from signal generator is applied between the probe tip and bottom electrode of specimen; the laser intensity reflected by the back of PFM cantilever will be detected by a photodiode detector, and the collected signals actually reflect piezoelectric vibration of specimen; signals are amplified by a lock-in amplifier connected with reference signals from the bottom electrode of the specimen [91, 92]. In this work, scanning probe microscope (Fig. 3.8) was used to determine the morphology and domain pattern at the interfacial zone of the composites. Ferroelectric domains images were obtained using customer-built piezoresponse force microscopy (PFM) based on a commercial atomic force microscope (SPA 400, Seiko Inc., Japan) and a commercial tip-cantilever system (Pt) with spring constant of 20 Nm⁻¹ was used.



Fig 3.7 The schematic of piezoresponse force microscopy [4]

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Fig 3.8 Piezoresponse force microscope (SPA 400, Seiko Inc., Japan)

3.4 Electrical properties measurements

Three types of material properties of composite, dielectric ferroelectric and piezoelectric are measured in this experiment.

3.4.1 Dielectric measurement

Figure 3.9 shows the experiment set up to measure the dielectric constant and dielectric loss tangent. The dielectric properties of sintered specimen were examined by LCR meter with frequency range from 1 kHz to 100 kHz at room temperature. The LCR-meter (HP 4194A, Hewlett-Packard Inc.) was measured the capacitance (C) and loss tangent (tan δ) of the samples at the frequency for 1 kHz. For dielectric constant, it could be obtained by using the following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{3.3}$$

where, *C* is capacitance of the sample, ε_r is the dielectric constant of the sample, ε_0 is the permittivity of vacuum (8.854×10⁻¹² F m⁻¹), *A* is the area of the electrode of the sample and *d* is the thickness of the sample respectively.



Fig 3.9 The experiment set up for dielectric properties measurements at room temperature

3.4.2 Ferroelectric measurement

The room temperature ferroelectric hysteresis (P-E) loops were characterized using a computer controlled Sawyer-Tower circuit [27] (Fig 3.10). The electric field was applied to a sample by a high-voltage ac amplifier with the input sinusoidal signal with a frequency of 20-100 Hz from a signal generator after the pellet composites were coated with high purity silver paint. During the polarization measurement, an electric field of 10-40 kV/cm based on the coercive fields was applied to a sample which immersed in a silicone oil to prevent the breakdown of the sample.



Fig 3.10 Schematic circuit of Sawyer-Tower bridge for the observation of P-E characteristics in ferroelectrics [27]

3.4.3 Piezoelectric measurement

The piezoelectric constant was measured by a static (or quasi-static) [27]. In the static method for measuring piezoelectric constant, the sample not in the vibration state during measurement. When a static measurement is performed, an external force of a certain magnitude is applied to the sample in a fixed direction; consequently, charges accumulate at the sample's surface owing to deformation of the sample by piezoelectric effect. These accumulated surface charges have a magnitude (per unit area) exactly equal to the electric displacement per unit volume. Moreover, there are other techniques also available for measuring piezoelectric constant. The principle of a quasi-static method is as follows. An alternating pressure of low frequency is applied on a piezoelectric sample and a standard (the piezoelectric constant d_{33} of which is known), while the concurrent charges from the sample with those from standard, the volume of d_{33} is computed and directly displayed on the screen. In this experiment, quasi-static d_{33} meter, model PM25, is used. See figure 3.11.



Fig 3.11 The d₃₃ meter model PM25

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