CHAPTER 5

EXPERIMENTAL PROCEDURE

This chapter details the experimental work on the synthesis and processing of PZT powders, ceramics and thick films, and characterisation of their microstructure and electrical properties are described. Detailed information about the raw materials used, sample preparation procedures and conditions and characterisation techniques are given.

5.1. Hydrothermal Synthesis of PZT Powders

5.1.1. Powder Synthesis

5.1.1.1. Raw materials

The basic raw materials for the preparation of PZT powders were lead acetate trihydrate, zirconium acetate solution and tetra-iso-propyltitanate. In a set of experiments, PbO and TiO_2 were used to examine the effect of precursor types on PZT formation. Lanthanum acetate hydrate and niobium oxalate were used as doping precursors in the PZT composition to improve its piezoelectric properties. The specifications of the chemicals used in the study are listed in Table 5.1.

$Pb(OAc)_2$ was an analytic grade powder with ash content > 99.5% and impurity content (Ca, Cl, Cu, Fe, Mg, Zn, etc.) < 5 ppm, which has a very good solubility in water. $ZrO(OAc)_2$ was an

acidic solution of zirconium acetate with pH3, containing the equivalent of 22.5 wt. % ZrO_2 and 17.0 wt.% CH_3COO^- according to the manufacturer. TIPT was modified with acetylacetone in order to prevent it from rapid hydrolysis during feedstock preparation. A clear solution was obtained when stirring acetylacetone with TIPT in a molar ratio of 2:1 at room temperature for 4 hours, which could be stored at room temperature for three months without hydrolysis. This reaction was reported to stabilise the metal alkoxides against precipitation or gelation [Yamamoto and Kamakawa, 1957]. Therefore, when the TIPT-AcAc precursor was added to $Pb(OAc)_2$ or $ZrO(OAc)_2$ aqueous solution, the hydrolysis reaction did not occur immediately. $La(OAc)_3$ was a highly hygroscopic powder with good solubility in water. Nb oxalate used in this study was a mixture of $X_3NbO(C_2O_4)_3$ and $X_2NbO(OH)(C_2O_4)_2$ ($X = NH_4^+$ or H^+). The dried Nb oxalate was slightly hygroscopic and was soluble in water.

5.1.1.2. Feedstock preparation

Two procedures have been used to prepare the hydrated mixed feedstock which are schematically shown in Fig. 5.1.

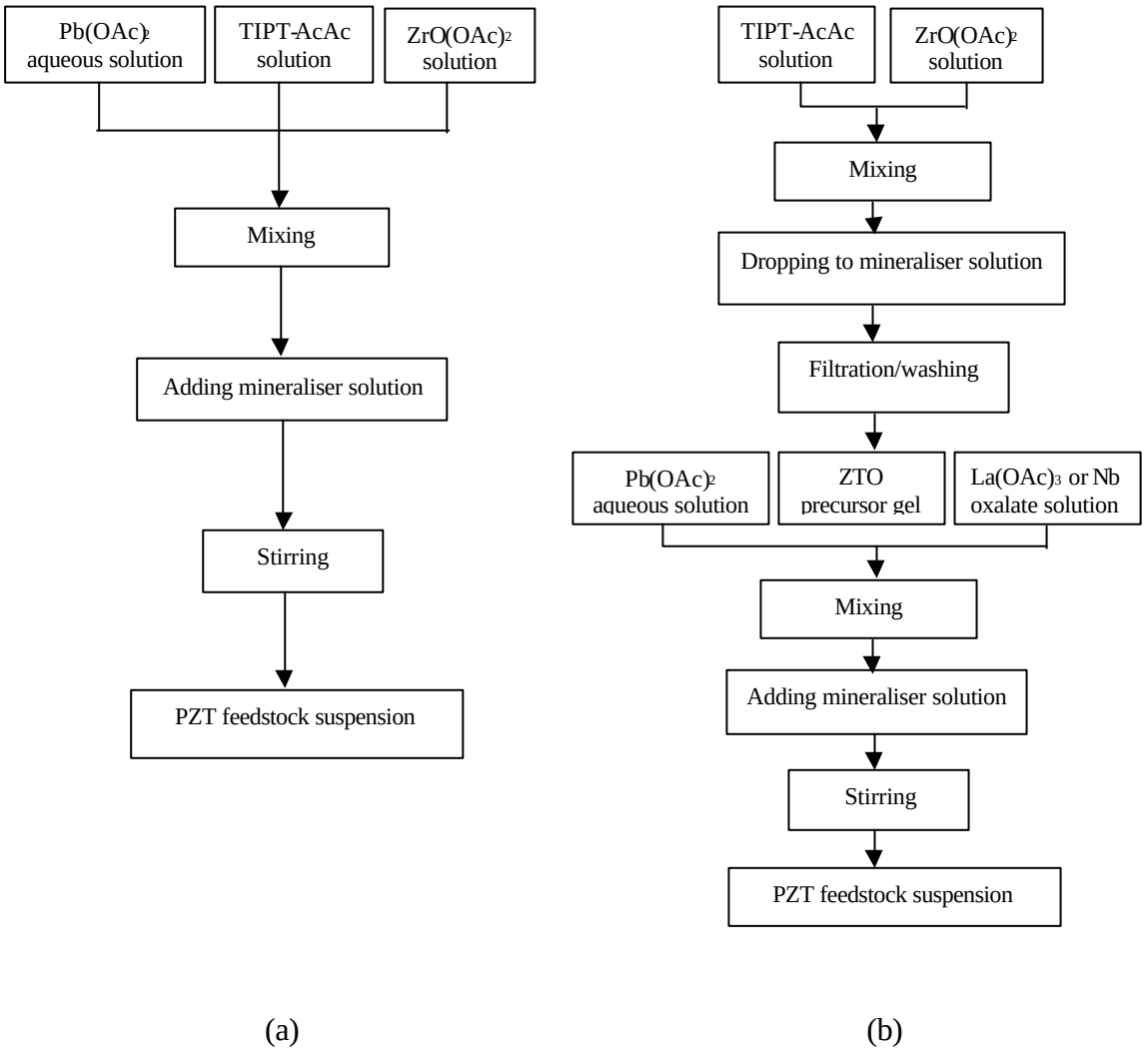
In the one-step procedure, lead acetate aqueous solution, zirconium acetate solution, and TIPT-acetylacetone solution were mixed and stirred in the ratio theoretically necessary to obtain the desired $Pb(Zr_{0.52}Ti_{0.48})O_3$ composition. The precipitation was performed by adding different base solutions (i.e. KOH, NaOH, $NH_3(aq)$, and $(CH_3)_4NOH$) in different concentrations (0.1 to 10 M).

Table 5.1. Specifications of the raw materials used in hydrothermal synthesis of PZT powders.

Components	**Chemicals**	**Formula**	**Molecular Weight or Weight %**	**Denotation**	**Manufacturer**
Pb precursor	lead acetate trihydrate	$Pb(CH_3COO)_2.3H_2O$	379.33	$Pb(OAc)_2$	Fisher, UK
	lead oxide	PbO (yellow)	223.19	PbO	Fluke, UK
Ti precursor	tetra-iso-propyltitanate	$Ti(CH(CH_3)_2)_4$	284.26	TIPT	Tioxide, UK
	titanium oxide	TiO_2	79.90	TiO_2	Tioxide, UK
Zr precursor	zirconium acetate solution	unknown	Zr content equivalent to 22.5 wt. % of ZrO_2	$ZrO(OAc)_2$	MEL Chemicals, UK
Dopant	lanthanum acetate hydrate	$(CH_3)_3$ La .xH_2O, $x \leq 2$	316.05	$La(OAc)_3$	Aldrich, UK
	niobium oxalate	$X_3NbO(C_2O_4)_3$ + $X_2Nb(OH)(C_2O_4)_2$, $X = NH_4^+$ or $X = H^+$	Nb: 20.7 wt. % C_2O_4: 54.7 wt. % NH_3: 5.0 wt. %	Nb oxalate	H. C. Starck, Germany
Mineraliser	potassium hydroxide	KOH	56.11	KOH	Aldrich, UK
	sodium hydroxide	NaOH	40.00	NaOH	Aldrich, UK
	tetramethylammonium hydroxide	$(CH_3)_4NOH$	91.15/25 wt. % solution in water	TMAH	Aldrich, UK
	ammonium aqueous solution	NH_3	17.03/35 wt. % NH_3 in water, S.G. 0.88	NH_3 (aq)	Fisher, UK
Modifier	acetylacetone	$CH_3COCH_2COCH_3$	100.12	AcAc	Fluke, UK

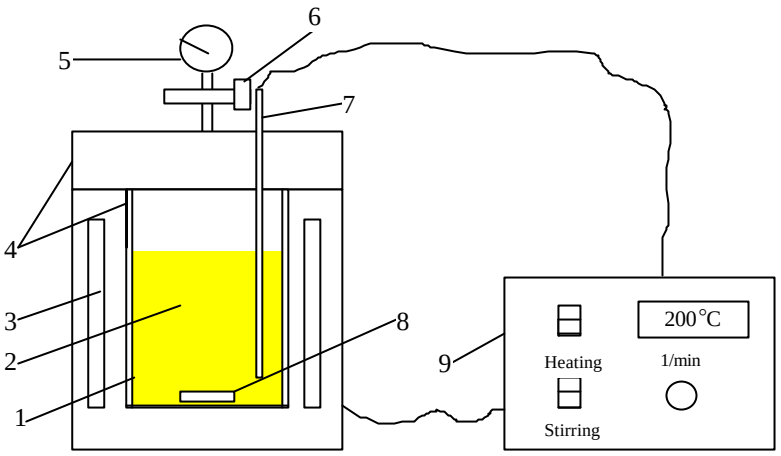
In the two-step procedure, a zirconia-titania precursor gel (ZTO) was prepared initially by mixing the TIPT-acetylacetone solution with the zirconium acetate solution together and then adding the resultant solution drop-wise into a 1 M KOH or NaOH aqueous solution to ensure the simultaneous precipitation of each cation. The co-precipitate was washed with deionised water and filtrated. In the second step, the washed ZTO precursor gel was mixed with lead precursor solution in the ratio theoretically necessary to obtain the desired $Pb(Zr_{0.52}Ti_{0.48})O_3$ composition.

Lanthanum acetate or niobium oxalate aqueous solution was used as a doping precursor and mixed with PZT precursor solution during the feedstock preparation. The molar content for both dopants was equivalent of 0.01 in the PZT composition. Finally, an amount of base mineraliser was added to the above solution to give a number of slurries with a base concentration ranging from 0.1 M to 1.0 M. The feedstock was then ready for hydrothermal treatment.



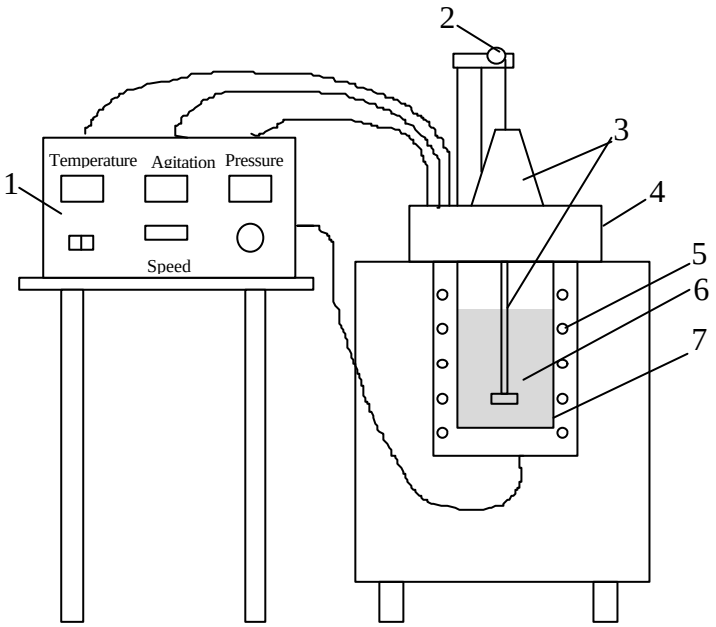
(a) (b)

Fig. 5.1. Two feedstock preparation procedures: (a) one-step and (b) two-step procedure.



1. PTFE cup; 2. Feedstock; 3. Heater; 4. Autoclave; 5. Pressure gauge; 6. Pressure releasing valve; 7. Thermocouple; 8. Magnetic stirrer; 9. Temperature and stirring controller.

(a)



1. Temperature and agitation controller; 2. Lifting motor; 3. Motor-driven magnetically-coupled stirrer; 4. Vessel lid; 5. Heating element; 6. Feedstock; 7. Ni-alloy vessel.

(b)

Fig.5.2. Diagram of autoclave apparatus: (a) low-temperature (< 200°C) autoclave; (b) high-temperature (> 200°C) autoclave.

5.1.1.3. Hydrothermal treatment

Hydrothermal synthesis of the PZT powders was performed under autogeneous pressure either in a PTFE-lined 250 ml autoclave (see Fig. 5.2 (a)), equipped with a magnetically stirrer/follower system (Berghof, Germany) or in a 4 litre corrosion-resistant nickel based superalloy (HASTALLOY C276) autoclave (see Fig. 5.2 (b)), equipped with a mechanically-driven magnetically-coupled stirring unit (Baskerville, UK) depending on the chosen synthesis temperature range. The synthesis temperature varied from 100°C to 350°C with holding time ranging from 2 hours to 30 hours. When the synthesis temperature was below 200°C, the 250 ml-autoclave was used with a stirring rate of about 750 revolution per minute. The total volume of the feedstock was kept constant at 230 ml. The as-prepared feedstock was charged into the autoclave and heated to temperatures of up to 200°C producing an autogeneous pressure of up to about 2 MPa. When the synthesis temperature required was above 200°C, the 4 litre-autoclave was used at a constant stirring rate of 500 revolution per minute and a constant heating rate of 3°C/ min. The volume of the feedstock was kept at 1.5 litre. The pressure build-up in the autoclave as a function of temperature is shown in Fig. 5.3.

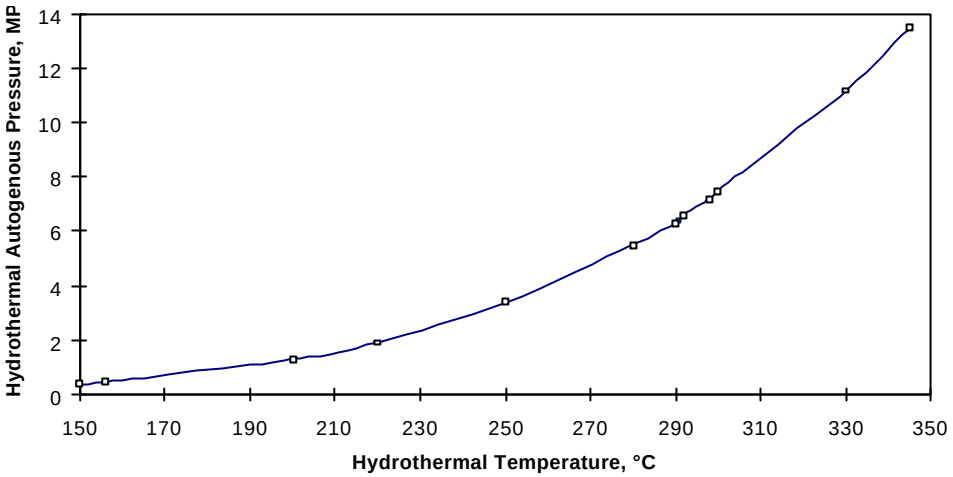


Fig. 5.3. The dependence of the autogeneous pressure on the hydrothermal temperature.

In order to investigate the formation mechanism of the PZT powders, samples of the reaction products were extracted through a specially designed valve at various temperatures and times during the synthesis process. The solid portion was separated from the extracted suspensions by centrifugation or sedimentation. Both the solid powders and the liquid supernatants were kept for subsequent characterisation. After cooling down, the product was either centrifuged, filtered or sedimented out, depending on the particle size (i.e. in order of increasing particle size), and washed successively with deionized water until the filtrate was pH neutral. About 13 to 15 g and 75 to 90 g PZT powders were obtained per batch from small and large autoclave, respectively, corresponding to about 80 to 90% of the theoretical yield. Finally, the wet powders were freeze dried in a freeze dryer (Modulyo, Edwards ,UK).

5.1.2. Powder Characterisation

5.1.2.1. Thermal analysis (TGA-DTA)

Thermal analysis was used to detect the weight loss and endothermic or exothermic changes of the hydrothermal PZT powders at various synthesis conditions. It was carried out on a simultaneous TGA-DTA apparatus (Stanton Redcroft STA-780) in both a stationary air and a flowing argon atmosphere at a heating rate of 10°C/min.

5.1.2.2. Evolved gas analysis (MS)

Evolved gas analysis was performed using a quadrupole mass spectrometer (VG G.A.S.) in connection with the TGA-DTA apparatus to determine the species responsible for the observed weight loss on TGA curves.

5.1.2.3. Fourier-transform infrared spectroscopy (FT-IR)

The nature of the functional groups of the reaction products which were extracted at various stages during the hydrothermal synthesis process of PZT powders was characterised by FT-IR spectroscopy (Nicolet 520). Samples was prepared for FT-IR analysis by mixing 10 wt. % hydrothermal powder with 90 wt. % KBr powder, and were analysed using a reflection mode.

5.1.2.4. X-ray diffraction (XRD)

Crystallographic and phase analyses were performed on an X-ray diffractometer (Hiltonbrooks DG2-2, UK) by using monochromatic CuKα radiation. The detection range was 20 to 60 degrees with a step size of 0.05° and a speed of 2°/min. Identification of crystalline phases was carried out by comparison of XRD patterns with JCPDS standards.

5.1.2.5. Transmission electron microscopy (TEM)

The particle size, morphology and chemical composition were characterised by transmission electron microscopy (TEM), using an instrument equipped with an energy dispersive X-ray spectroscopy analyser (Philips CM 20 TEM with a Link 6586 EDX analyser). TEM characterisation was performed using bright field imaging, selected area diffraction (SAD) and energy dispersive X-ray (EDX) analysis. The TEM samples were prepared by dispersing a powder sample in ethanol using ultrasonic agitation, then picking up some of the powder particles on a 100-square-mesh copper grids, pre-coated with a thin carbon film.

5.1.2.6. Scanning electron microscopy (SEM)

The particle size and morphology were also characterised by high-resolution field emission microscopy (Hitachi 4000 FEG SEM) and conventional scanning electron microscopy (JEOL JSM 5410 SEM). The powder samples were embedded in a conductive graphite adhesive fixed to an aluminium stub and then gold-coated with a Polaron E5000 sputter-coating unit for 2 minutes.

5.1.2.7. Particle size analysis

The particle size distribution was measured using a laser diffraction particle size analyser (Coulter LS 130, UK), whose detection limit was claimed to be above 0.1 μm by the manufacturer. The samples were prepared by dispersing the PZT powders in deionized water containing 2 wt. % dispersant (A40, $[-CH_2CH(COO^-NH_4^+)-]_n$, Allied Colloids, UK) using a high intensity ultrasonic probe (VCX 600, Sonics and Materials Inc., USA). The optical model used for calculating the

particle size distribution was based on the refractive indices of each component. Taking an average of the refractive index of ZrO_2 as 2.40, TiO_2 as 2.50, and PbO as 2.61 [Weast *et al.*, 1984], the real part of the PZT optical model was then taken as 2.53, and the imaginary part was taken as zero due to its light pale colour [Coulter, 1990]. Both the differential and cumulative particle size distributions were calculated in terms of the number and volume percentage.

5.1.2.8. Inductively coupled plasma (ICP) spectroscopy

The solubility of the lead, titanium, zirconium and potassium or sodium in the hydrothermal solution was measured by inductively coupled plasma (ICP) spectroscopy (PU 7450). The samples were the supernatants extracted from the autoclave.

5.1.2.9. Electrophoretic mobility measurements

The surface charge of the hydrothermal PZT powders was characterised by measuring the particle electrophoretic mobility. Measurements were conducted on a Doppler electrophoretic light scattering analyser (Coulter Delsa 440) using 1 vol. % powder suspension samples. All measurements were done in the presence of 0.01 M KNO_3 aqueous solution in order to suppress the effect of the counter-ions on the particle electrophoretic mobility. The pH was adjusted by the addition of dilute (0.1 M) KOH or HNO_3 solution. The pH was measured by a calibrated Gallenhamp pH stickmeter.

5.1.2.10. Powder density measurements

The relative density of the powder was measured using a relative density bottle (Fig. 5.4) in conjunction with the following formula:

$$\text{Relative density} = \frac{\text{mass of powder}}{\text{mass of same volume of water}} = \frac{m_3 - m_1}{(m_2 - m_1) - (m_4 - m_3)} \quad (5.1)$$

where m denotes a mass measurement.

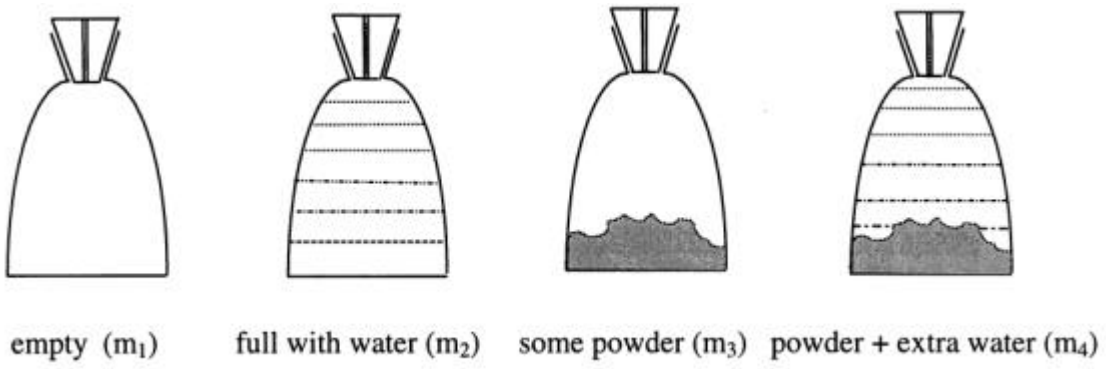


Fig. 5.4. Schematic diagram showing the measurements required in the density bottle method [After Akrill *et al.*, 1973].

5.2. Processing of PZT Ceramics and Thick Films

5.2.1. Dry Powder Pressing

5.2.1.1. Materials

Two types of PZT powder were used in this study. Six hydrothermal PZT powders synthesised under different conditions were used in comparison with two mixed-oxide powders. The specification of each of the PZT powders is listed in Table 5.2. Polymer binder was used in the

dry pressing to increase the green strength. The binder system was a non-aqueous polyvinyl butyral (PVB)/cyclohexanone solution.

Table 5.2. Specifications of the PZT powders used in dry pressing

PZT Powder	**Synthesis Route**	**Composition and Synthesis Conditions (The basic composition is $Pb(Zr_{0.52}Ti_{0.48})O_3$)**
HS-6	hydrothermal	undoped, 2 M KOH, 200°C/2 hours, one-step feedstock
HS-36	hydrothermal	undoped, 4 M KOH, 200°C/0.5 hour, one-step feedstock
HT-29	hydrothermal	undoped, 0.4 M KOH, 300°C/2 hours, two-step feedstock
HT-34	hydrothermal	1 mol % Nb, 0.4 M KOH, 300°C/2 hours, two-step feedstock
HT-35	hydrothermal	1 mol % La, 0.4 M KOH, 300°C/2 hours, two-step feedstock
HT-37	hydrothermal	0.6 mol % Nb, 0.4 M KOH, 300°C/2 hours, two-step feedstock
PZT-5A*	mixed-oxide	unknown doping, mixing, jet milling, calcination
MO-PZT*	mixed-oxide	2 mol % Nb, mixing, ball milling, calcination

* PZT-5A and MO-PZT are two mixed-oxide PZT powders from Morgan Matroc (Verniton, Southampton, UK) and self-made respectively.

5.2.1.2. Processing

The binder was introduced with the powder in a weight ratio of about 0.5% by mixing using a mortal and pestle. After the evaporation of solvent, green disc compacts were pressed in a one-action die with diameter of 13 mm using an Avery-Denison mechanical testing machine (Denison Meyer Group, UK). The pressure applied was 100 MPa. In a set of experiment, the pressures ranging from 30 to 100 MPa were applied to examine the effect of compaction pressure on green density. Debinding was carried out at a heating rate of 1°C/min to 600°C and held for 2 hours

before sintering. The green density was calculated from the weight and dimensions of the compact.

5.2.2. Viscous Polymer Processing (VPP)

5.2.2.1. Polymer system

The key of this processing is to use polymer solutions which can give exactly the right visco-elastic behaviour when mixed with fine ceramic powders. An aqueous polymer system was used in this study. The specification of each component is listed in Table 5.3.

Table 5.3. Specifications of the polymer system used in viscous polymer processing

Component	Role	Denotation	Formula	Manufacturer
polyvinyl alcohol-acetate	binder	KH 17S	$[\text{-}CH_2CH(OH)\text{-}]_m$-$[\text{-}CH_2CH(COOCH_3)\text{-}]_n$	Nippon Synthetic Chemical Industry Co. Ltd, Japan
methyl cellulose	binder			Dow Chemicals, USA
glycerol	dispersant		$HOCH_2CH(OH)CH_2OH$	Fluke, UK
deionised water	solvent		H_2O	

5.2.2.2. VPP processing

Viscous processed green compacts were prepared by mixing PZT powders with the above polymer system in a water-cooled twin-roll milling machine (Winkworth Machinery Ltd, UK) for about 30 minutes. The amount of the polymer was adjusted to ensure the “dough” having an optimum rheology for effective agglomerate breakdown as well as good sheet-forming ability. The resultant green sheet was then placed between two steel plates in a hydraulic press at a pressure

of about 1 MPa for 24 hours for de-airing. Disc samples were subsequently cut from the sheet using a cork borer and then dried between two flat plaster plates at 40°C for 12 hours. Debinding was carried out in an oven using a heating rate of 1°C/min and a holding temperature of 600°C for 2 hours before sintering. Two PZT powders, i.e. PZT-5A and HT-37, were used.

5.2.3. Direct Coagulation Casting (DCC)

5.2.3.1. Dispersion of aqueous PZT suspension

The dispersion behaviour of the PZT powder in aqueous suspension was observed by measuring the sedimentation height of the suspension in a sample tube with the sedimentation time as a function of pH and dispersant. The dispersant used was diammonium citrate (DAC, $NH_4OOCCH_2C(OH)(COOH)CH_2COONH_4$, Sigma, UK). The PZT powders used were PZT-5A and HT-37. All suspensions were dispersed under an agitation of an ultrasonic probe (VCX 600, Sonics and Materials Inc., USA) at a power level of 30 % in pulse mode (1 second on/0.5 second off) for less than 5 minutes in an ice bath to reduce the heating effect generated during dispersion. The pH values of the suspension were adjusted using a 0.1 M HNO_3 or KOH solution.

The surface charge of PZT particles in suspension was studied through the measurement of electrophoretic mobility (Coulter Delsa 440) on powder suspension of 1 vol. % of dispersion medium, in the presence of 0.01 M KNO_3 aqueous solution as a buffer in the dispersion medium, in order to suppress the effect of counter ions on the electrophoretic mobility.

The viscosity measurements of suspensions with a solids loading ranging from 20 to 60 vol. % of dispersion medium were made with a controlled stress rheometer (Carri-Med CSL 500) using a cone-plate arrangement. The measurement temperature is 10°C and the shear stress and shear rate range is 3000 dyne/cm^2 and 1500 1/second, respectively.

5.2.3.2. DCC of aqueous PZT suspension

A lactone (δ-gluconolactone, Aldrich, UK) was used to shift the pH from 6 to 4 by hydrolysis. Urease and urea (Sigma, UK) was used as an enzyme-substrate system to increase the ionic strength in order to coagulate the suspension by an internal reaction.

Suspensions with solids loading from 50 to 60 vol. % of dispersion medium and 0.5 wt. % DAC of the PZT powder as a dispersant were prepared by dispersing under ultrasonic agitation in an ice bath. Removal of entrapped air was carried out in a vacuum chamber for about 30 minutes before casting the suspension into a silicone rubber mould. Drying was performed in a controlled humidity chamber at room temperature and about 80 % relative humidity.

5.2.4. Processing of PZT Thick Films

5.2.4.1. Electrophoretic deposition (EPD)

Two hydrothermal PZT powders (HT-29 and HT-37) were used in EPD processing. Suspension of PZT powder from 0.5 to 5 wt. % concentrations of dispersion medium (water) were prepared by dispersing the powder in an aqueous solution with 2 wt. % DAC of the PZT powder as a dispersant using ultrasonic agitation. A schematic diagram of the EPD apparatus is shown in Fig. 5.5. Two electrodes were placed parallel at a separation distance of 2 mm in the suspension. A stainless steel plate and a substrate (Pt wire or Pt coated alumina) were attached to the negative and positive electrodes, respectively, since the particle surface was shown to be negatively charged by the electrophoretic mobility measurements. A DC voltage of 4 V was applied between the elecrtrodes in the static suspension. The deposition time varied from 10 seconds to 30 minutes.

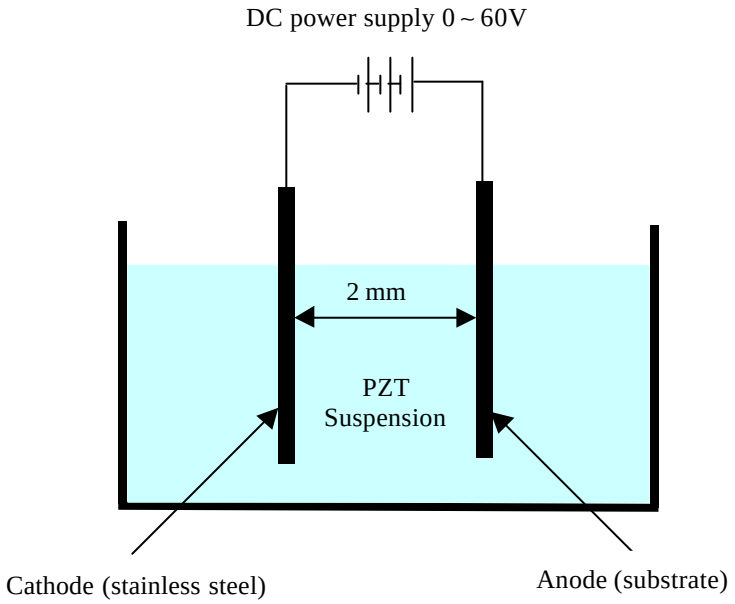


Fig. 5.5. A schematic diagram of EPD apparatus for PZT thick films.

5.2.4.2. Screen printing

The slurry used in screen printing was prepared by mixing a hydrothermal PZT powder (HT-37) with a non-aqueous ink system (63/2 medium, Cookson and Matthey Ceramics and Materials Ltd., UK)) in a three-roll mill (Marchant, UK). A solids loading of about 30 vol. % of ink was obtained in the slurry with reasonably low viscosity for screen printing, due to the fine particle size and large surface area of the hydrothermal PZT powder. Screen printing was performed with standard screen printer (MPM, USA) on a 96% pure alumina substrate with a thickness of 1.5 mm (Hybrid Laser Tech., UK). Drying was carried out in oven at 40°C for 2 hours before sintering.

5.2.5. Sintering of Bulk PZT Ceramics and Thick Films

The above prepared green compacts and films were placed in a closed alumina crucible, in which the specimens were embedded in a ZrO_2 bed separated by coarse ZrO_2 powders; and surrounded by PZT powder which was used for the PbO atmosphere buffer. Sintering was carried out in a tube furnace under stationary air atmosphere using a heating rate of 1°C/min at different temperatures from 750°C to 1250°C for different holding times from 5 minutes to 2 hours. In order to examine the effect of sintering atmosphere, a dynamic oxygen (flowing rate: 200 cm^3/min) was also used in a set of experiment.

The sintering behaviour in air was monitored via a differential dilatometer (Netzsch, Geratebau GmBH, Germany), using a sapphire reference and a heating rate of 10°C/min.

The specimen weight loss and linear shrinkage during sintering were measured. The sintered density of specimens was determined using Archimedes' method using following formula:

$$\rho = \frac{W_1}{W_2 - W_3} \qquad (5.2)$$

where W_1 is the dry weight of the sample, W_2 represents the damp weight which is measured after the sample was heated in boiling water to drive off the air in the open pores and the surface water was wiped off, and W_3 represents the wet weight measured when the sample is immersed in water.

5.3. Microstructure Characterisation and Electrical Property Measurement

5.3.1. Phase Identification and Microstructure Characterisation

The phases present after sintering were identified by powder XRD using CuKα radiation (Hiltonbrooks DG2-2, UK). The sintered microstructure was studied by SEM (JEOL JSM5410), using both polished and thermally etched sections and fractured surfaces. Thermal etching was performed at 1000°C, both in air without PZT buffer and in air with PZT buffer for several minutes. The composition of the sintered sample was studied by EDX (AN 10000) on polished surface. The sample was coated with a carbon film using a carbon coater (Polaron TB 500, UK).

5.3.2. Measurements of Dielectric and Piezoelectric Properties

Silver paste electrodes were spray-painted and fired on both sides of the specimens in air at 600°C for 10 min. The specimens were poled under a DC field of 2.5 kV/mm in a mineral oil bath at 120°C for 10 min in order to accelerate the poling process.

All the measurements were performed after the poling treatment, using an impedance analyser (4194A, Hewlett Packard, USA). The relative permittivity ε_r was measured at a frequency of 1 kHz. The electromechanical coupling coefficient K_p and the mechanical quality factor Q_m were measured by a resonance-antiresonance method [IRE standards, 1961]. The equations used for calculating ε_r, Q_m and K_p were (2.3), (2.4) and (2.6), respectively.