# CHAPTER 3

# EXPERIMENTAL PROCEDURES

The experimental techniques adopted for the preparation and characterization of the ceramics in this study are described in this chapter, with detailed presentation of each technique for selected mixed normal-relaxor ferroelectric ceramics. In the *x*PZN - (*1-x*)PZT series, six different compositions were prepared via different techniques. The processing study of PZN-PZT was divided into two parts. The first was the "classic" solid state mixed oxide method; and the second, the columbite-wolframite precursor method. In the *x*PZT - (*1-x*)PNN series, the ceramics were prepared by the columbite-wolframite precursor method, with *x* varying from *0.5 – 0.9* . In the ternary PNN-PZN-PZT system, the composition *0.5*PNN-(*0.5-x*) PZN-*x*PZT was selected for this study. The compositions synthesized in this study were *x* = *0, 0.1, 0.3*, and *0.5* in the ternary system. All powder compositions were prepared by the columbite-wolframite precursor method.

## 3.1 Powder preparation

Polycrystalline ceramic materials investigated in this study were prepared using the solid-state mixed oxide method and columbite-wolframite precursor methods. The chemical purity and suppliers are listed in Table 3.1 For PZN-PZT, the raw materials used for the solid solution were regagent grade lead oxide (PbO), zirconium dioxide ($ZrO_2$), Zinc oxide (ZnO), niobium pentaoxide ($Nb_2O_5$), and Titanium dioxide ($TiO_2$). For the PNN-PZT system, the raw materials used in the columbite-wolframite precursor approach were PbO, $ZrO_2$, $Nb_2O_5$, $TiO_2$ and nickel oxide (NiO). NiO, $TiO_2$, $ZrO_2$ and $Nb_2O_5$ were readily available sources for the $Ni^{2+}$, $Ti^{4+}$, $Zr^{4+}$and $Nb^{5+}$, respectively. PbO was initially chosen as the $Pb^{2+}$ cation source. In the last composition, for the PNN-PZN-PZT system, the raw materials used in columbite-wolframite precursor approaches were PbO, $ZrO_2$, $Nb_2O_5$, $TiO_2$, NiO and ZbO. The mixing process, schematically illustrated in Fig. 3.1, was employed as a routine processing procedure for all powder preparation in this work. In the mixing process, the starting oxides were batched according to the formula, and intimately mixed in a ball mill with polyethylene jars for 24 hours using isopropyl alcohol (IPA) and ½" $ZrO_2$ balls as grinding media. The slurry dish was dried on a hotplate with a magnetic stirring action to prevent gravitational separation of the components. It was then put into an air oven at 80 °C/24-36 hours. The dried mixture was ground, sieved and calcined in double alumina crucibles. The double crucible technique was used in this method to prevent PbO volatilization (Fig. 3.2).

For reduction of the powder's grain size, and its increase in surface area, the calcined powder was ball milled for 6 hours. After the 2nd calcination, the calcined powder was dried and sieved.

**Table 3.1** Specifications of the component oxide powders used in this study.

| Materials | Purity (%) | Formula weight | Manufacturer |
|---|---|---|---|
| Lead(II)oxide<br>PbO | 99.99 | 223.189 | Fluka Chemical<br>GmbH, Switzerland |
| Zirconium dioxide<br>$ZrO_2$ | 99.90 | 123.223 | RdH laborchemikalin<br>GmbH&Co.KG,France |
| Titanium dioxide<br>$TiO_2$ | 99.99 | 79.898 | RdH laborchemikalin<br>GmbH&Co.KG,France |
| Zinc(II)oxide<br>ZnO | 99.90 | 81.389 | Fluka Chemical<br>GmbH, Switzerland |
| Nickel(II)oxide<br>NiO | 99.99 | 74.693 | Fluka Chemical<br>GmbH, Switzerland |
| Niobium<br>pentaoxide<br>$Nb_2O_5$ | 99.99 | 265.807 | Aldrich Chemical<br>Company Inc., USA |

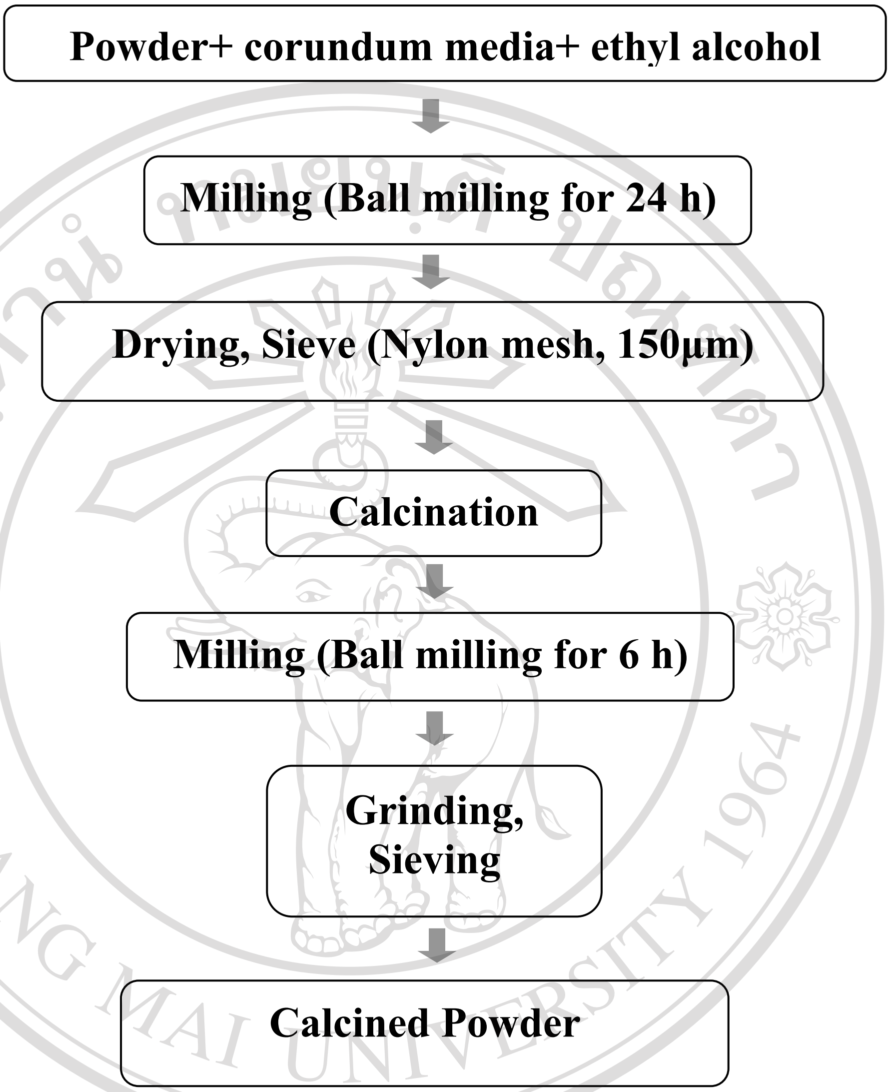

**Figure 3.1** Mixed and Calcination Processes (MCP) for powder preparation.

### 3.1.1 Preparation of the PZN-PZT system

Since both PZT and PZN have a perovskite structure and are known to have excellent dielectric and piezoelectric properties, it was suggested to alloy PZN with PZT to stabilize and optimize the PZN ceramics. This study aimed to provide a comprehensive examination of the process-property relationships in the binary system of PZN–PZT with a wide composition range. Both the conventional mixed-oxide and columbite precursor method have been used in synthesizing the PZN–PZT ceramics.

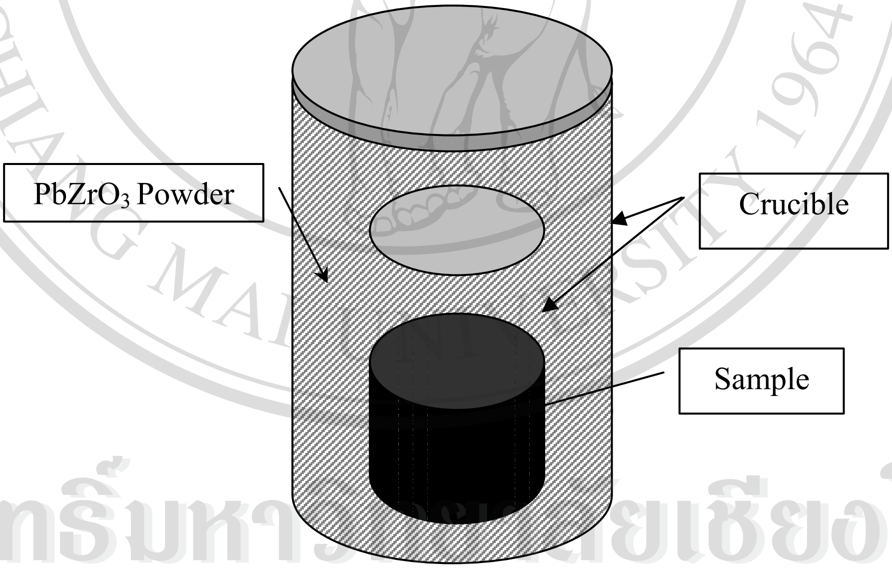

**Figure 3.2** The double crucible technique.

The conventional method utilized a one-step reaction with all starting materials, whereas the columbite method was used as an initial step for preparing the columbite precursor ($ZnNb_2O_6$) and wolframite precursor ($ZrTiO_4$), followed by a reaction with PbO to form the PZN–PZT ceramics.

### 3.1.1.1 Solid-state mixed oxide method

The solid-state mixed oxide method is the traditional technique for producing oxide ceramics. It simply involves batching stoichiometric amounts of constituent oxide precursors, mixing and milling the powders and calcining the mixture that is at an appropriate temperature. Many perovskite normal ferroelectrics and antiferroelectrics can be produced by this method. Complex perovskite materials have proven difficult to produce via the mixed oxide method. The PZN-PZT powders were prepared using a traditional mixed oxide synthesic route as shown in Fig. 3.3. The raw materials used in the mixed oxide approach were PbO, ZnO, $Nb_2O_5$, $ZrO_2$ and $TiO_2$. The starting oxides were batched according to the following formula:

$$PbO(s)+ZnO(s)+ZrO_2(s)+TiO_2(s)+Nb_2O_5(s) \text{----->} xPb(Zn_{1/3}Nb_{2/3})O_3\text{-}(1\text{-}x)Pb(Zr_{1/2}Ti_{1/2})O_3(s)$$

In stoichiometric amounts, a 2 mol% excess of PbO was added to compensate the weight loss during calcinations and the sintering process. A mixing process for the preparation of PZN-PZT powder was performed according to 3.1. The mixture was calcined at temperatures between 750 and 950°C for 4h in a double crucible configuration. A heating rate of 20°C/min was selected for all of the compositions in this system.

### 3.1.1.2 Columbite-wolframite precuresor method

The columbite precuresor method was developed by Swartz and Shout[20] for producing $Pb(Mg_{1/3}Nb_{2/3})O_3$. It essentially comprised two mixed oxide reaction states as follows: in the first stage, ZnO was reacted with $Nb_2O_5$ to give $ZnNb_2O_6$, which had a columbite structure. The columbite phase, $ZnNb_2O_6$, was synthesized according to the following formula:

$$ZnO(s)+Nb_2O_5(s)\rightarrow ZnNb_2O_6(s)\ \text{(columbite)}$$

and the wolframite $ZrTiO_4$ was synthesised by $ZrO_2$ reacted with $TiO_2$. The columbite phase, $ZrTiO_4$, was synthesized according to the following formula:

$$ZrO_2(s)+TiO_2(s)\rightarrow ZrTiO_4(s)\ \text{(wolframite).}$$

The mixture process described in 3.1 was followed. Calcining temperatures of 975°C for 4 hours and 1,400°C for 4 hours were chosen for the $ZnNb_2O_6$ precursor and $ZrTiO_4$, respectively. X-ray diffraction analysis showed that the materials were essentially single-phase after the calcination process for both precursors.

PZN-PZT was formed by adding PbO to the $ZnNb_2O_6$ and $ZrTiO_4$ precursors according to the following formular:

$$PbO(s)+ZnNb_2O_6(s)+ZrTiO_4(s)\rightarrow xPb(Zn_{1/3}Nb_{2/3})O_3-(1\text{-}x)Pb(Zr_{1/2}Ti_{1/2})O_3(s)\ \text{(perovskite).}$$

A schematic diagram of the powder preparation route for $ZnNb_2O_6$, $ZrTiO_4$ and PZN-PZT powder is illustrated in Fig. 3.4. In all compositions, 2 mol% excess PbO was added to compensate for lead volatilization during calcination and sintering. The mixture was calcined at temperatures between 750 and 950$^o$C for 4h in a double crucible configuration. A heating rate of 20$^o$C/min was selected for all of the compositions in this system.  X-ray diffraction was used to determine the amount of perovskite phase present after calcining.

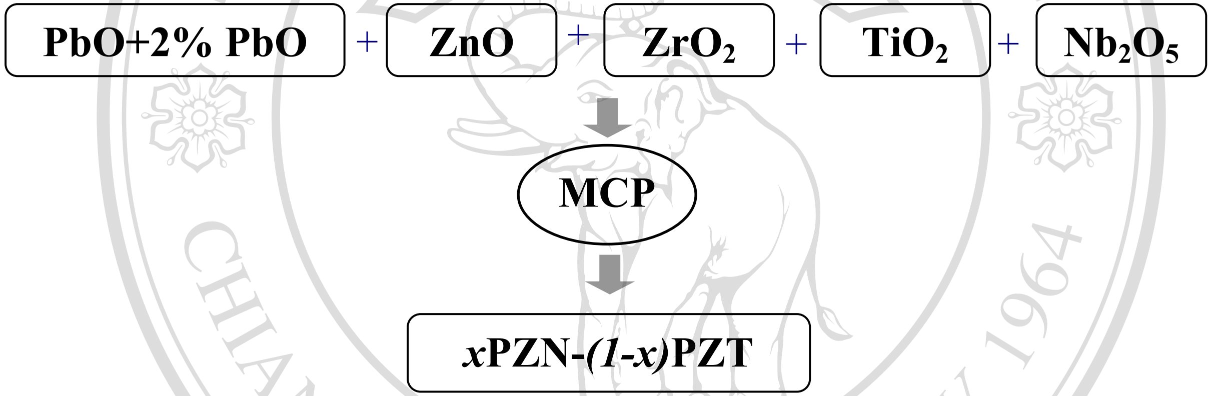

**Figure 3.3** the processing flow chart for the PZN-PZT powder.

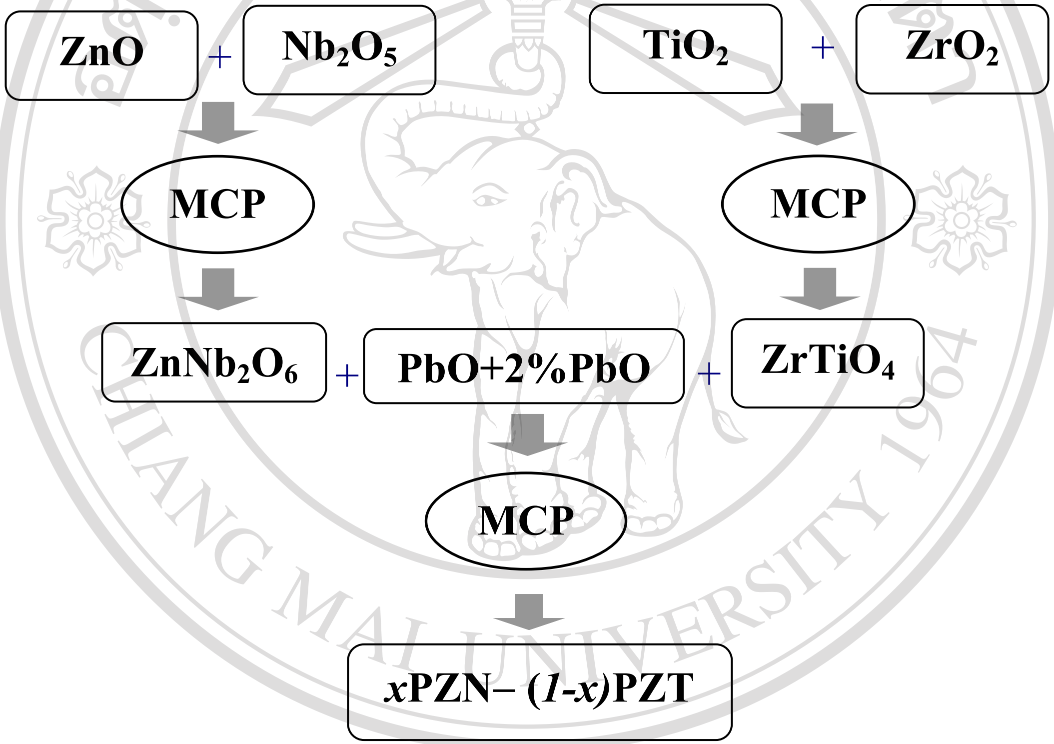

**Figure 3.4** Columbite-wolframite precursor for binary solid solution PZN-PZT.

### 3.1.2 Preparation of PNN-PZT powders

Since PNN is a relaxor ferroelectric, with a broad dielectric peak near $T_c \approx -120^{\circ}C^{41}$ and PZT (Zr/Ti = 50/50) and sharp maximum permittivity at $T_c \sim 390^{\circ}C^{2}$, the Curie temperature in the PNN-PZT system can be engineered over a wide range of temperatures by controlling the amount of PZT in the system. The aim of this work was to investigate the quasi-binary solid solution, $x$PZT (Zr/Ti = 50/50) – $(1-x)$PNN, with $x$ = 0.4 - 0.9. Although pure PNN-PZ-PT ternary ceramics can be fabricated by conventional methods, the B-site precursor method is a better one for enhancing the dielectric and ferroelectric properties.

This process involves pre-reacting the B-site cations to form the columbite phase, $NiNb_2O_6$, and the wolframite phase, $ZrTiO_4$. With this method it is possible to obtain a homogeneous perovskite solid solution without the other constituent perovskite phases such as PZ, PT, PZT and PNN, and the formation of the parasitic pyrochlore phases is prevented. Finally, the nature of the relaxor-normal ferroelectric phase transition was studied through a combination of dielectric measurements and x-ray diffraction. For PNN-PZT, the columbite, $NiNb_2O_6$, was systhesized according to the following formula:

$$NiO(s)+Nb_2O_5(s)\rightarrow NiNb_2O_6(s) \text{ (columbite).}$$

The mixture process described in 3.1 was followed. A calcining temperature of 1,100°C for 4 hours and 1,400°C for 4 hours was chosen for the $NiNb_2O_6$ and $ZrTiO_4$ precursor, respectively. X-ray diffraction analysis showed that the materials was essentially single-phase after the calcination process for both precursors. PNN-

PZT was formed by adding PbO to the $NiNb_2O_6$ and $ZrTiO_4$ precursor according to the following formular:

$PbO(s)+NiNb_2O_6(s)+ZrTiO_4(s) \rightarrow x\text{Pb}(Zr_{1/2}Ti_{1/2})O_3 - (1\text{-}x)\text{Pb}(Ni_{1/3}Nb_{2/3})O_3$ (s) (perovskite).

A schematic diagram of the powder preparation route for $NiNb_2O_6$, $ZrTiO_4$ and PZN-PZT powder is illustrated in Fig. 3.5. In all compositions, 2 mol % excess PbO was added to compensate for lead volatilization during calcination and sintering. The mixture was calcined at a temperature of 950°C for 4h in a double crucible configuration. A heating rate of 10°C/min was selected for all of the compositions in this system. X-ray diffraction was used to determine the amount of perovskite phase present after calcining.

### 3.1.3 Preparation of PNN-PZN-PZT powder

In this study, the perovskite phase formation and stability in the ternary solid solution was $0.5$PNN–$(0.5–x)$PZN–$x$PZT, where $x = 0.1 – 0.5$ had been investigated. The columbite method was used to successfully prepare single-phase perovskite PNN–PZN–PZT ceramics. The process of pre-reacting the B-site cations forming the columbite phases, $ZnNb_2O_6$ and $NiNb_2O_6$, and wolframite phase, $ZrTiO_4$, was used to eliminate other constituent perovskite phases such as PZ, PT, PZT, PNN, and limit formation of the parasitic pyrochlore phases.

In this method, the columbite precursors, $ZnNb_2O_6$ and $NiNb_2O_6$, were prepared from the reaction between ZnO and $Nb_2O_5$ at 975°C for 4 hours and between

NiO and $Nb_2O_5$ for 4 hours at 1,100°C, respectively. The wolframite phase, $ZrTiO_4$, was formed by reacting $ZrO_2$ with $TiO_2$ at 1,400°C for 4 hours.

The powders of $ZnNb_2O_6$, $NiNb_2O_6$, and $ZrTiO_4$ were mixed in the required stoichiometric amounts with PbO, with an excess of 2 mol% of PbO added according to the following formular:

$$PbO(s)+NiNb_2O_6(s)+ZnNb_2O_6(s)+ZrTiO_4(s) \rightarrow \mathit{0.5}Pb(Ni_{1/3}Nb_{2/3})O_3–\mathit{(0.5\text{-}x)}Pb(Zn_{1/3}Nb_{2/3})O_3–xPb(Zr_{1/2}Ti_{1/2})O_3(s)\ \text{(perovskite).}$$

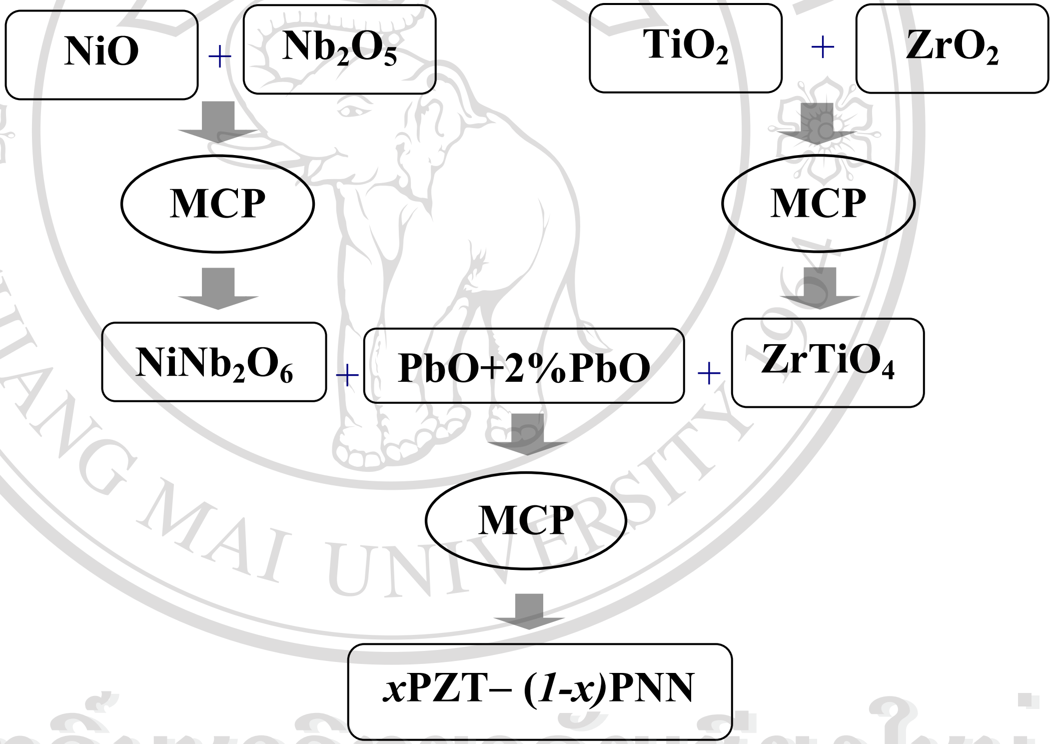

**Figure 3.5** Columbite-wolframite precursor for binary solid solution PZT-PNN.

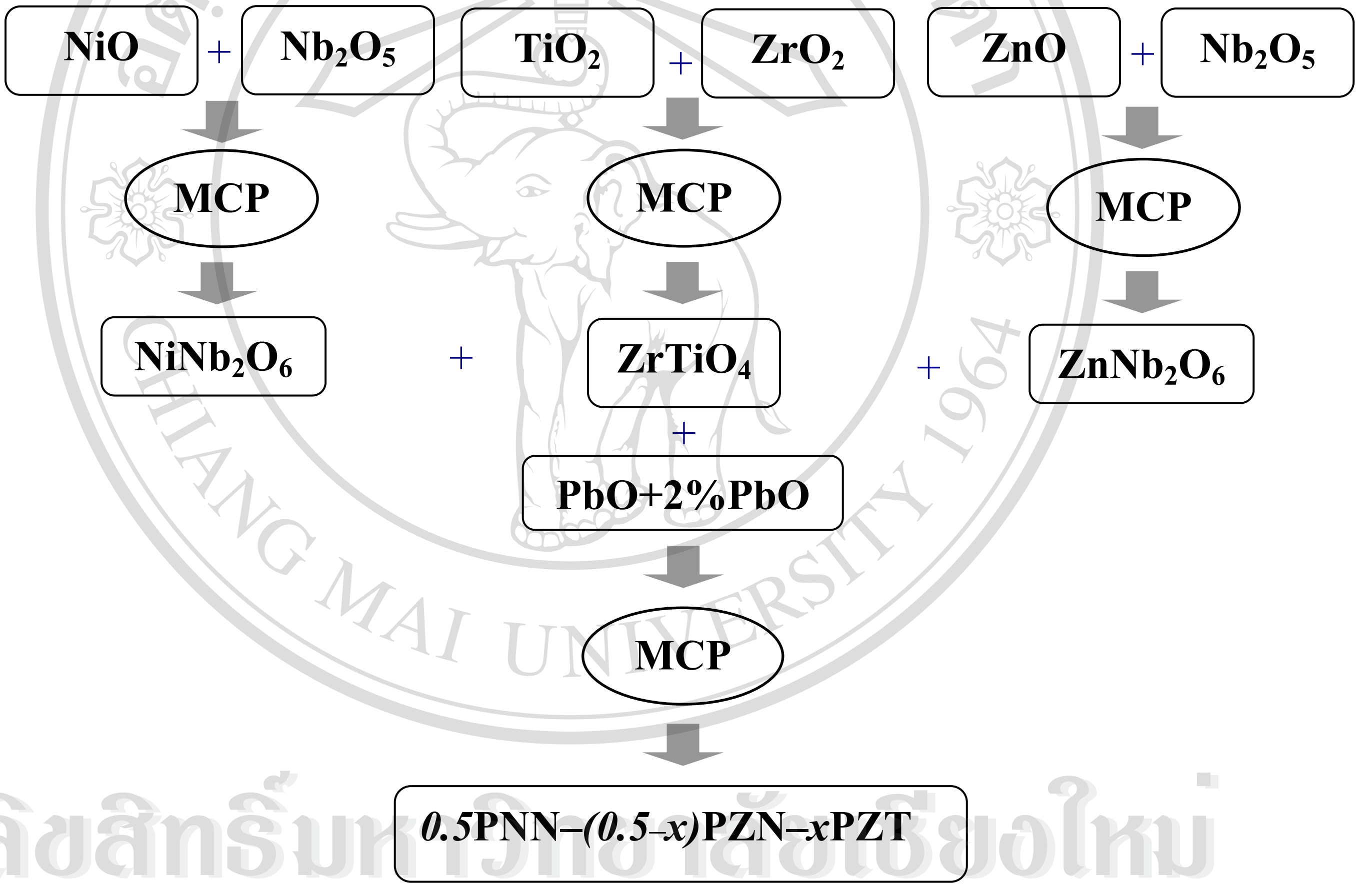

**Figure 3.6** Columbite-wolframite precursor for binary solid solution, PNN-PZN-PZT.

The compositions synthesized in this study were $x = 0$, $0.1$, $0.3$, and $0.5$ in the ternary system, $0.5$PNN–$(0.5–x)$PZN–$x$PZT. A schematic diagram of the powder preparation route for $NiNb_2O_6$, $ZrTiO_4$ and PZN-PZT powder is illustrated in Fig. 3.6. In all of the compositions, 2 mol% excess PbO was added to compensate for lead volatilization during calcination and sintering. The mixed powders were calcined at 900 – 950$^{o}$C for 4 hours in a double crucible configuration, with a heating rate of 20$^{o}$C/min. X-ray diffraction was used to determine the amount of perovskite phase present after calcining.

## 3.2 Ceramic processing

After calcination, the calcined powder (~2.5 g) was mixed with 5 wt% poly (vinyl alcohol) binder. Discs with a diameter of 1.5 cm and a thickness of 2 mm were prepared by cold uniaxial pressing at a pressure of 60 MPa. Binder burnout occurred by slowly heating (1$^{o}$C/min) to 500$^{o}$C and holding for 2 hours.

For the PZN-PZT system, five sintering conditions were selected for use, with a range for both methods of 1,175°C, 1,200°C, 1,225°C, 1,250°C, and 1,275°C, and a dwell time of 2 hours. For the binary PNN–PZT system, sintering occurred between 1,100 – 1,250$^{o}$C, with a dwell time of 4 hours. Regarding investigation of the sintering behavior of the ternary PNN-PZN-PZT system, the discs were sintered in a sealed alumina crucible at temperatures ranging from 950$^{o}$C – 1,250$^{o}$C using a heating rate of 5$^{o}$C/min and a dwell time of 2 hours.

To prevent PbO volatilization from the pellets, a PbO atmosphere was controlled with a bed of $PbZrO_3$ powder placed in the vicinity of the pellets. A double-inverted crucible technique was applied for all compositions, which contained an atmosphere of $PbZrO_3$ powder to prevent lead loss, as shown in Fig. 3.7. A small alumina crucible containing specimens and atmosphere powder was put on an alumina plate and covered by the alumina crucible, with the atmosphere of $PbZrO_3$ powder sealed into the gap between the crucible and plate.

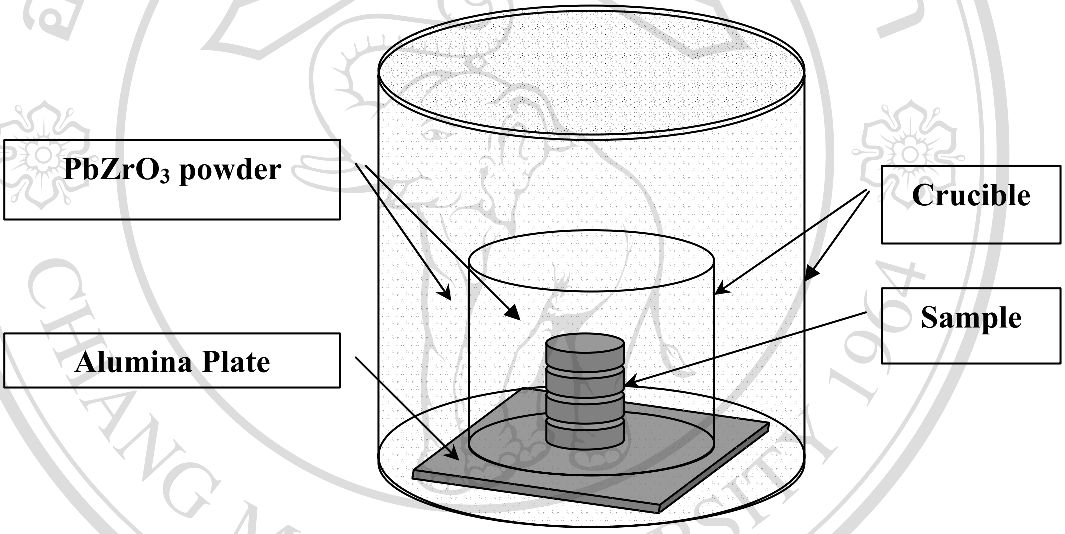

**Figure 3.7** Schematic diagrams showing the double-inverted crucible technique.

## 3.3 Structure characterization

### 3.3.1 X-ray diffraction (XRD)

To determine the phase purity and lattice parameters of calcined powder and ceramics samples, the x-ray diffraction technique was performed using an automated diffractometer employing Ni-filtered Cu-$K_\alpha$ radiation, with a tube voltage and current of 50 kV and 27 mA, respectively. The relative amounts of the perovskite and pyrochlore phase were estimated from the major peak intensity [(110) and (222)] of the respective phases. The percentage was calculated using the following equation:[20]

$$\%\ \text{Perovskite Phase} = \left(\frac{I_{\text{Perov}}}{I_{\text{Perov}} + I_{\text{Pyro}} + I_{\text{PbO}}}\right)\times 100 \qquad (3.1)$$

where ″ I ″ represents the intensity of the respective phases. The presence of the other phases was determined by comparing the XRD patterns with JCPDS fields.

### 3.3.2 Scanning electron microscopy (SEM)

The microstructure of sintered PZT ceramic samples was examined from photomicrographs of the thermally etched surfaces. Prior to thermal etching, the surfaces of sintered ceramics were ground and polished with the following increasingly fine grades of SiC polishing powder; 5 and 3 μm. Then the surfaces were finished with diamond paste to provide a mirror-like surface. Thermal etching of the polished samples was performed using a fast heating rate at temperatures below the 200°C sintering temperature, resulting in no grain growth during the thermal etching profile. The thermally etched surfaces were photomicrographed using scanning electron microscopy (SEM, JEOL JSM-840A). The surfaces of all the samples were gold-coated for 1 minute to prevent charging in the SEM. The average grain sizes were determined by using the circle intercept method, where random circles were drawn on the micrograph and the number of grain boundaries intercepting these circles counted.

### 3.3.3 Transmission electron microscopy (TEM)

A transmission electron microscope (TEM) was employed to investigate the domain and crystal structure of sintered ceramics as a function of composition. Samples for TEM were prepared by grinding and polishing the sintered ceramic samples to a thickness of ~ 70-100 μm using SiC paper. These were mounted on 7 mm copper grids using epoxy. Thin foils of the specimens were prepared to electron transparency by standard techniques, with a "dual-ion mill" operated at 5 kV at a 10° inclination. The foils were investigated by TEM (CM30, Philips, Eindhoven, The Netherlands) operated at a 200 kV accelerating voltage.

## 3.4 Property measurement

### 3.4.1 Electric field-polarization hysteresis

Polarization measurements were performed using an RT66A ferroelectric test system (Radiant Technologies) in virtual ground mode. The RT66A Standardized Ferroelectric Test System is specifically designed to perform the tests required for characterizing non-linear ferroelectric thin films or specific bulk ceramic devices. It combines the features of a function generator, an electrometer and a digital oscilloscope in a single package. The tester is controlled from an IBM PC or compatible computer system. The user specifies the operations to be performed by the tester from a menu driven interface. The RT66A software then executes the appropriate hardware commands, collects and processes the data, and then displays the results on the user's screen.

Prior to the measurement, samples were ground parallel and polished using a final grit of 3 μm alumina. They were cleaned with detergent and water and then acetone in an ultrasonic bath before electroding with sputtered gold. An air-dried silver paste was applied to the gold sputtered surfaces to insure good electrical contact. Copper wires were attached to both sides of samples using silver epoxy without clamping sample in order to provide free mechanical boundary condition. Dueing the polarization measurement, an electric field of 5-35 kV/cm based on the coercive fields was applied to a sample which has being immersed in a silicone oil to prevent the breakdown of the sample.

### 3.4.2 Dielectric measurements in normal atmosphere

The dielectric measurements were carried out on automated systems. The first system consisted of an LCR meter (HP 4824A, Hewlett-Packard Inc.), a computer controlled oven (model 9023 delta design Inc.), and a desktop computer. This system was capable of making dielectric measurements in the frequency range of 100 Hz-500 kHz and temperature range of -150$^{o}$C – 180$^{o}$C. When higher temperature measurements were requested, a high temperature measurement cell (NorECS Probostat) was used, as shown in Fig. 3.8. This instrument was designed to work from room temperature to 1,600°C. Prior to the measurements, the surfaces of the samples were polished with 3 μm $Al_2O_3$ powders and electroded by sputtering with gold. To ensure good electrical contact, air dry silver paste was applied over the gold electrode. The samples were heated at a standard rate of ± 2°C/min in air, while the capacitance and loss were measured using an applied ac voltage of 1 V at frequencies between 100 Hz to 500 kHz. The diameter of the samples was at least 10 times the thickness to avoid fringing filed effects. The relative permittivity "$\varepsilon_r$" was calculated by the following equation:

$$\varepsilon_r = \frac{Ct}{\varepsilon_o A} \tag{3.2}$$

where C is the capacitance (Farad), $\varepsilon_o$ the permittivity of free space (8.854 x $10^{-12}$ F/m), and A and t the electrode area and thickness of the sample in meters, respectively

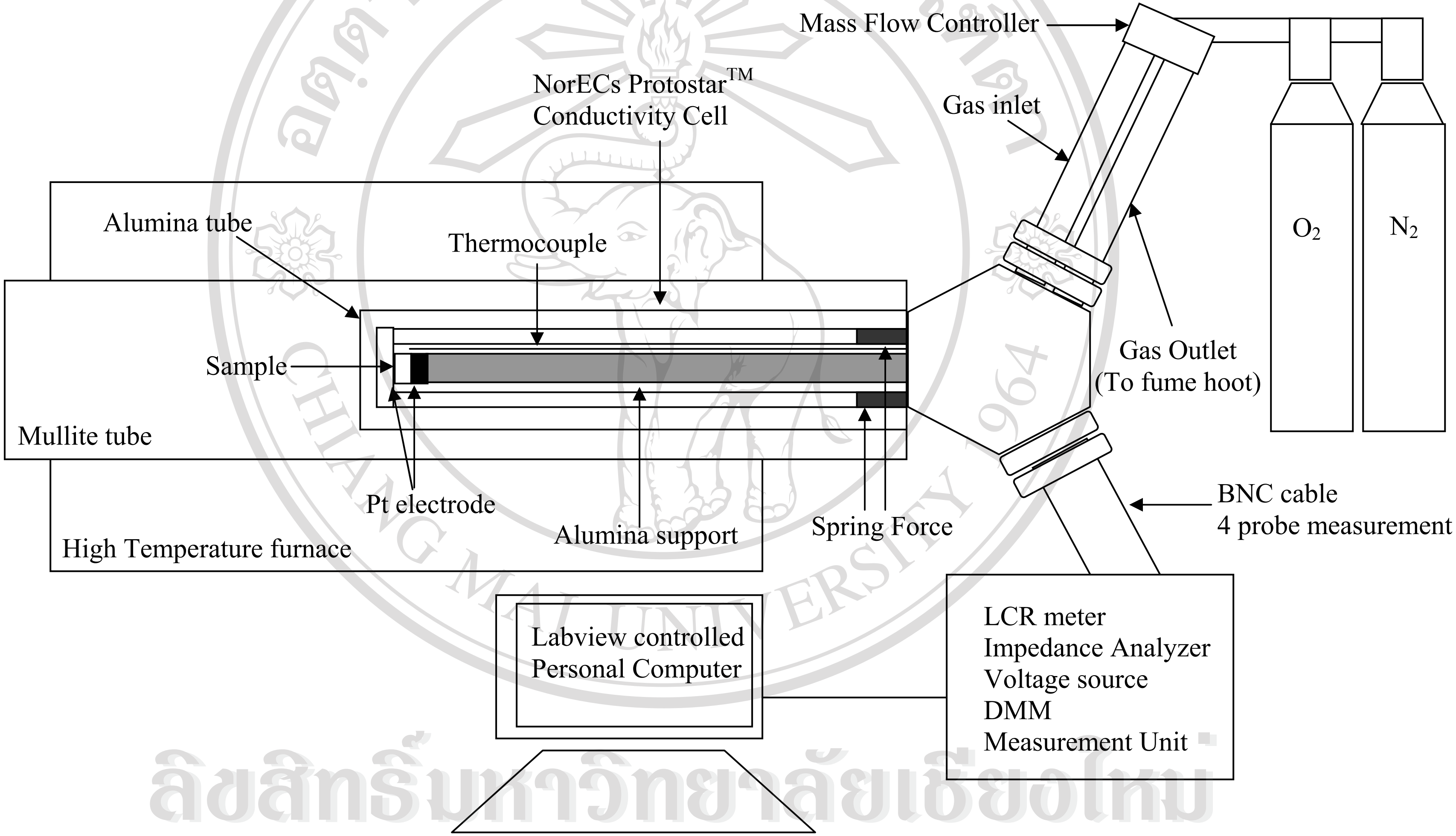

**Figure 3.8** Schematic diagram of sample holder for high temperature dielectric measurement.

### 3.4.3 Piezoelectric coefficients and electromechanical coupling factors

The piezoelectric coefficients and electromechanical coupling factor were determined as a function of composition for all ceramics systems. The techniques used were based on the IEEE Standard on Piezoelectricity (ANSI/IEEE Std.176-1987).

The piezoelectric constant, $d_{33}{}^{*}$, was measured, using a $d_{33}$ meter (8000 $d_{33}$ tester). Subsequently, one day old samples were poled. The electromechanical properties of poled ceramics were determined by resonance methods using an HP Impedance/Gain-phase Analyzer interfaced to a desktop computer. The IEEE Standards outline the methods required to calculate the electromechanical properties of specimens from the series resonance frequency and parallel resonance frequency of the impedance spectrum. They are commonly measured by determining the frequency difference between maximum (parallel anti-resonance, $\mathrm{f_a}$) and minimum impedance (series resonance, $\mathrm{f_r}$) of an electroded ceramic disk in the electrical resonance circuit. The piezoelectric planar coupling factor ($k_p$) is defined by the following equation:[2,13]

$$k_p = \sqrt{2.51\frac{\left(f_a^2 - f_r^2\right)}{f_r^2} + 0.038} \tag{3.3}$$

Prior to measurements, the gold-electroded samples were poled with an applied electric field of 20 to 30 kV/cm based on the coercive fields for 60 minutes while being in a silicone oil bath at a heat below the 30°C transition temperature. The samples were then cooled down to room temperature. Copper wires were attached to the gold-electroded surfaces of the samples by using silver epoxy.

---

* $\mathrm{d_{ij}}$: the first subscript refer to the direction of the electric field, the second one the direction of the strain.