CHAPTER 3

EXPERIMENTAL PROCEDURE

This chapter describes all the experimental procedures employed in this work to synthesis, fabricate and characterize the desired compositions. Although the materials and their manufacturing steps differ amongst themselves, many of the basic principles are similar.

3.1 Sample Preparation

The main purposes of preparation methods are generally to create materials of desired composition, which meet specific properties at an economic cost and an appropriate development time.

3.1.1 Powder preparation

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 suppliers, formula weights and purities. These oxides were re-checked by X-ray diffraction technique in order to determine their phase compositions and impurities.

Table 3.1 Specifications of the starting materials used in this study.

Powder	Source	Formula weight	Purity (%)
PbO	Fluka*	223.189	99.99
TiO_2	Riedel deHaen**	79.898	99.99
MgO	Fluka*	40.311	99.00
Nb_2O_5	Aldrich***	265.807	99.99

Note : * Fluka Chemical GmbH, Switzerland

** RdH Laborchemikalin GmbH&Co. KG, France

*** Aldrich Chemical Company Inc., USA

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 calculated relevant proportions of constituents were weighed, suspended in isopropyl alcohol (IPA) and intimately mixed in a McCrone vibro-mill, for 45 minutes with corundum media. Drying was carried out for 2 h (the sample dish was placed on a hotplate with a magnetic stirring in action to prevent gravitational separation of the components), prior to sieving through a 150 μm mesh. The dried powder was then ground, sieved and calcined in closed alumina crucribles.

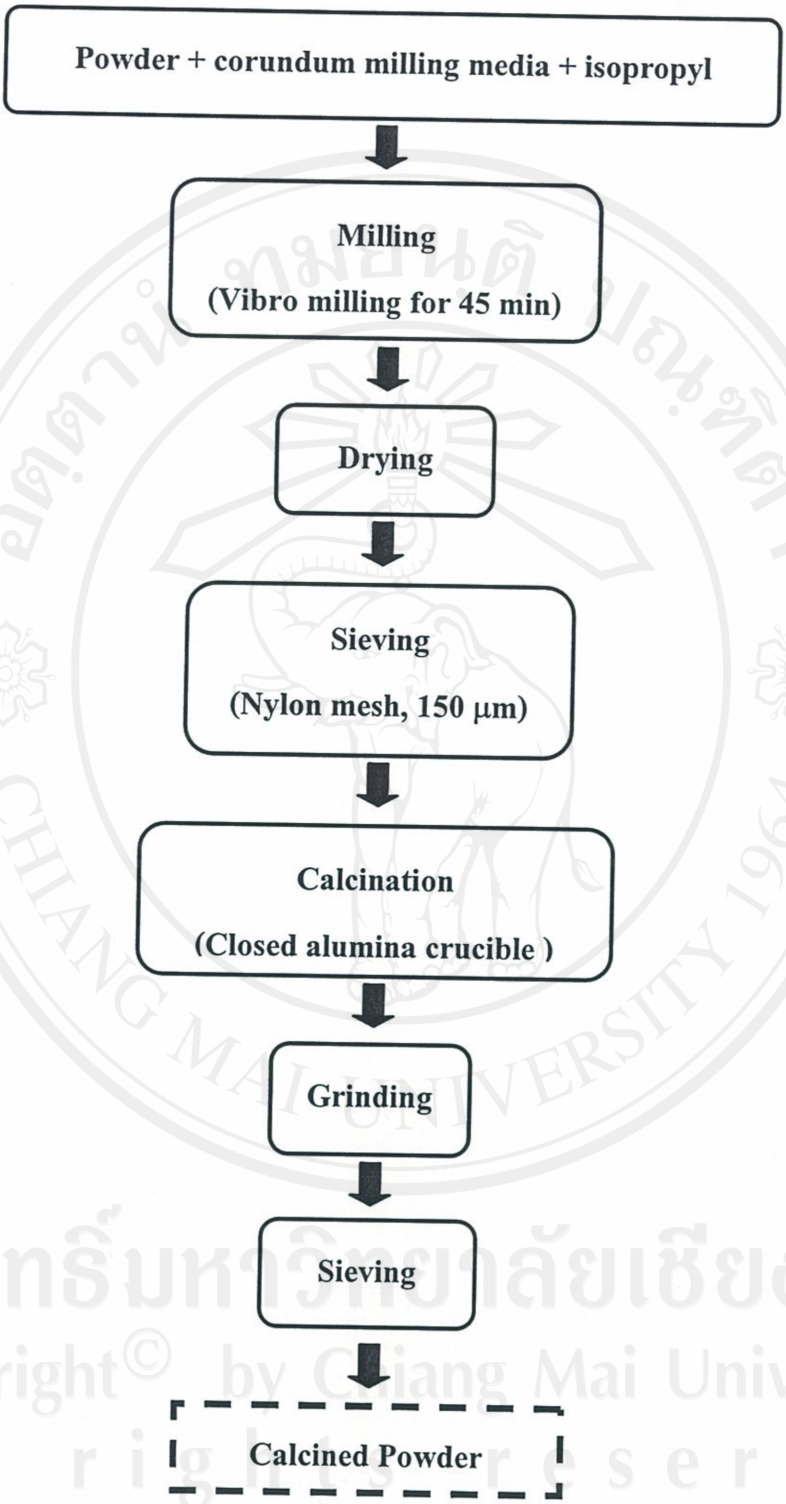

Fig 3.1 Mixing and calcination processes (MCP) for powder preparation.

3.1.1.1 Preparation of PMN powders

The columbite method was chosen as the basis for preparation of PMN powders. It essentially comprised two mixed oxide reaction stages as follows: in the first stage MgO was reacted with Nb_2O_5 to give $MgNb_2O_6$ (columbite-like phase), and in the second stage, PbO was reacted with the $MgNb_2O_6$ to give the final product of perovskite PMN.

Stage 1) $MgO + Nb_2O_5 \rightarrow MgNb_2O_6$ (3.1)

Stage 2) $3PbO + MgNb_2O_6 \rightarrow 3\,Pb(Mg_{1/3}Nb_{2/3})O_3$ (3.2)

The starting powders of PbO, MgO and Nb_2O_5 were used, and the mixing process described in 3.1.1 was followed. Conditions for optimising the calcination were carefully determined. A schematic diagram of the powder preparation route for $MgNb_2O_6$ and PMN powders is illustrated in Fig. 3.2.

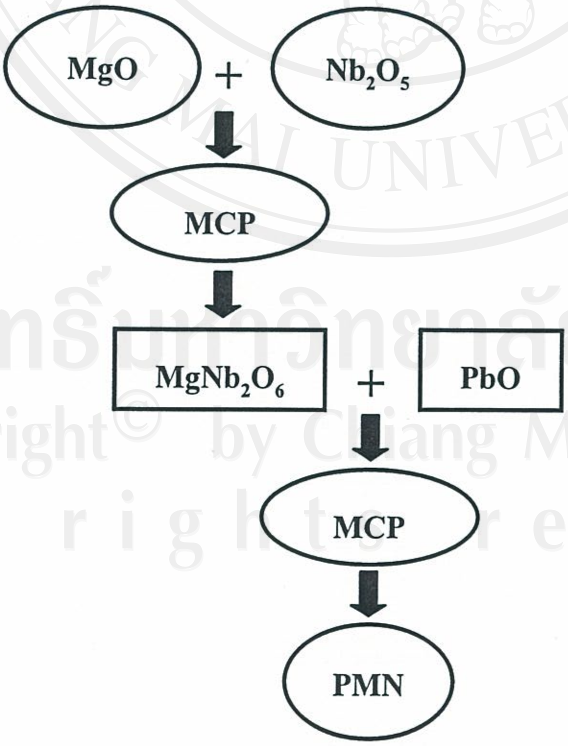

Fig. 3.2 Two-stage processing route for perovskite PMN powders.

3.1.1.2 Preparation of PT powders

Lead titanate powders were prepared using a simple mixed oxide synthetic route as shown in Fig. 3.3. This method comprised a solid-state reaction of lead oxide, (PbO) and titanium oxide, (TiO_2) as follows :

$$PbO + TiO_2 \rightarrow PbTiO_3 \tag{3.3}$$

Mixing process for the preparation of PT powders was performed according to 3.1.1. Conditions for optimising the calcination were also carefully determined.

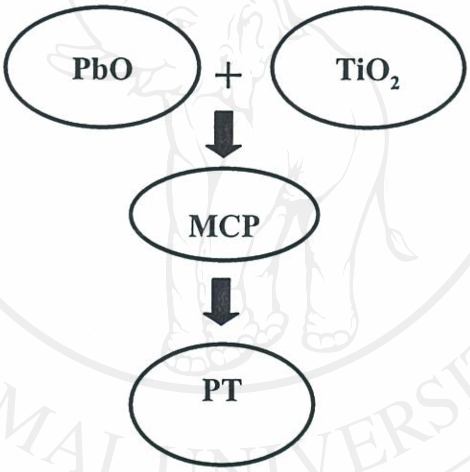

Fig. 3.3 Flow chart for the preparation of PT powders.

3.1.1.3 Preparation of (1-*x*)PMN-*x*PT powders

In this work, the system under investigation is (1-*x*)PMN-*x*PT with values of *x* ranging from 0.0 to 1.0 at regular steps of 0.1. Each composition was prepared by weighing required proportions of constituent chemicals, i.e. $MgNb_2O_6$ (from section 3.1.1.1), PbO and TiO_2. The mixing process described in 3.1.1 was followed. Conditions for optimising the calcination were carefully determined. A schematic diagram of the powder preparation route for (1-x)PMN-xPT powders is given in Fig. 3.4.

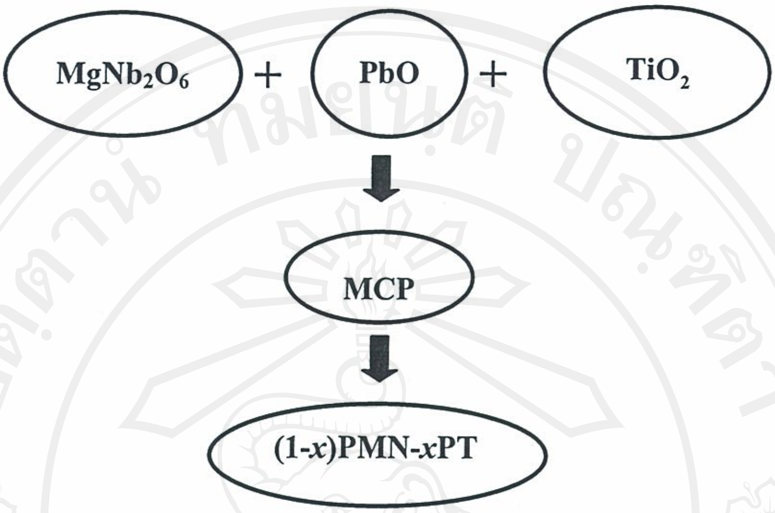

Fig. 3.4 Flow chart for the preparation of (1-x)PMN-xPT powders.

3.1.2 Ceramic fabrication

In this work, all ceramic compositions have been fabricated by uniaxial pressing the calcined powder (~ 2 g) of each composition into a green pellet of diameter 15 mm and sintered under the appropriate conditions in a high temperature furnace.

To aid pressing and green densification, 3 wt-% polyvinyl alcohol (PVA) binder was added into the calcined powders prior to pressing. After the binder was burnt out at 500 °C for 4 h, 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, taking care not to touch the pellet. The specimen arrangement is shown in Fig. 3.5. Alumina crucible was closed with an alumina lid before insertion into a high temperature sintering furnace.

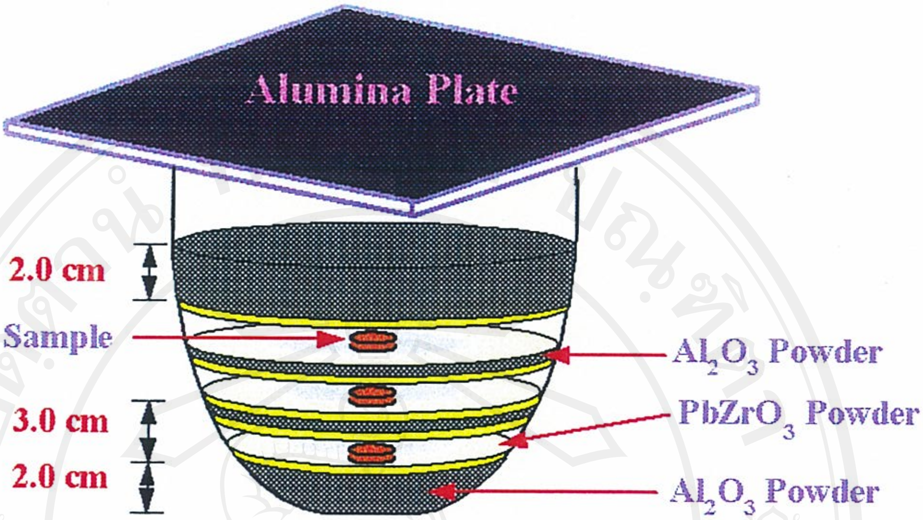

Fig. 3.5 Sample arrangement for the sintering process.

3.2 Sample Characterization

The following section is intended to address the main characterization techniques used to investigate the phase formation, morphology, particle size and microstructure of the materials in this study.

3.2.1 Thermal analysis (TG-DTA)

In this study, thermogravimetric and differential thermal analysis (TG-DTA) techniques were used to monitor the thermal behavior due to the reactions between the oxide precursors. They were carried out on the powder mixtures at a heating rate of 10 ^{o}C/min with a simultaneous thermal analyser (PERKIN ELMER Model TGA -7 and DTA-7, Germany) as shown in Fig. 3.6.

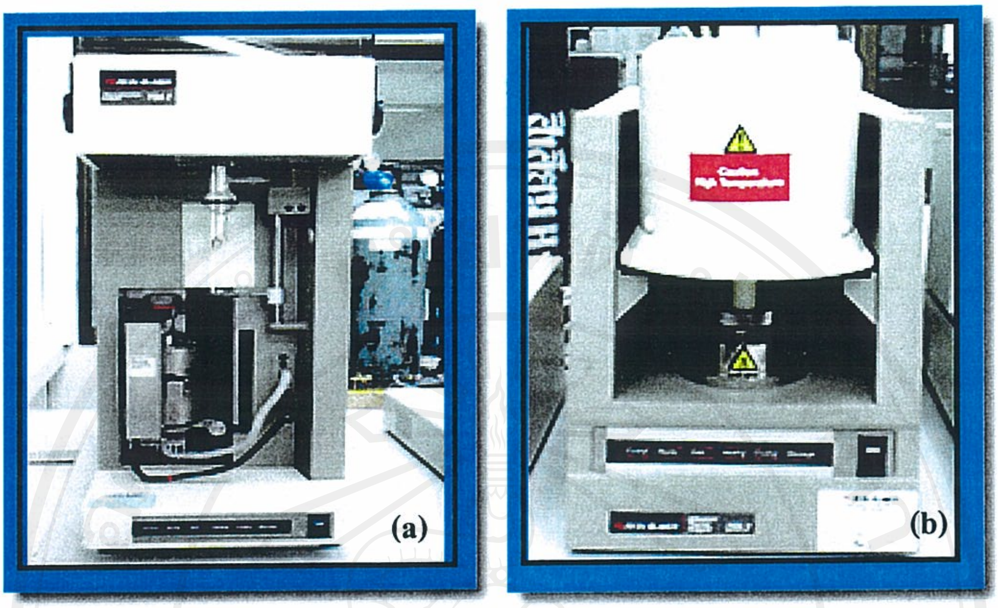

Fig. 3.6 Thermal analysers: (a) TG and (b) DTA.

3.2.2 The X-ray diffraction (XRD) technique

In this study, XRD was used to identify the optimum firing temperatures, for phase identification, for quantitative analysis of mixtures of phases, and also to determine the crystal structure of materials at room temperature, in both powder and ceramic forms. A Seamens-D500 diffractometer with Cu K_α radiation at 40 kV (Fig. 3.7) was employed. Lattice parameters of the materials were determined from XRD patterns.

The amount of the perovskite phase presents in each sample, in principle, was estimated using the following equation as suggested by Swartz and Shrout,[20] on the basis of relative intensities of the major reflections for the perovskite and pyrochlore phases :

$$Perovskite\ phase\ (wt\%) = \left(\frac{I_{per}}{I_{per} + I_{pyr}} \right) \times 100 \qquad (3.4)$$

This equation should be seen as a first approximation, since its applicability requires comparable maximum absolute intensities of the pair of perovskite and pyrochlore peaks being used. Here I_{per} refers to the intensities of the {110} perovskite peak and I_{pyr} to the intensity of the {222} pyrochlore (e.g. $Pb_3Nb_4O_{13}$ or $PbTi_3O_7$) peak, these being the most intense reflections in the XRD patterns of both phases. This equation has been widely used in connection with the preparation of perovskite materials.[7,141]

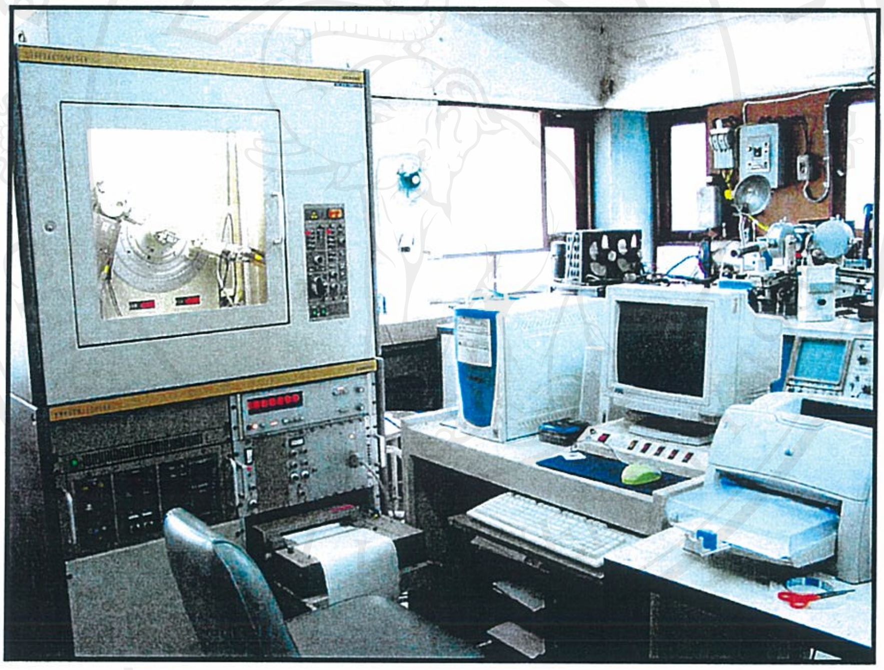

Fig. 3.7 X-ray diffractometer.

3.2.3 Scanning electron microscopy (SEM)

In this work, the particle sizes and morphologies of the powders, the as-fired (or free) and fracture surfaces of sintered ceramics have been directly imaged using two scanning electron microscopes, one a JEOL JSM-840A (Fig. 3.8) and the other a Hitachi S-700 SEM (Department of Material Science, University of Leeds, Leeds

U.K.). Both were interfaced to a digital image capture system, and fitted with an energy-dispersive X-ray (EDX) analyser with an ultra-thin window (Oxford Instruments).

In particle size range of the calcined powders was estimated from SEM micrographs. Average grain sizes of the sintered ceramics were estimated by using linear intercept method,[113] where random lines were drawn on a micrograph and the number of grain boundaries intercepting these lines counted. Grain shape of sintered ceramics was classified by using the concept of degree of angularity under the ASTMD 2488-90.[114] EDX was employed to determine the chemical compositions of the selected area of the samples.

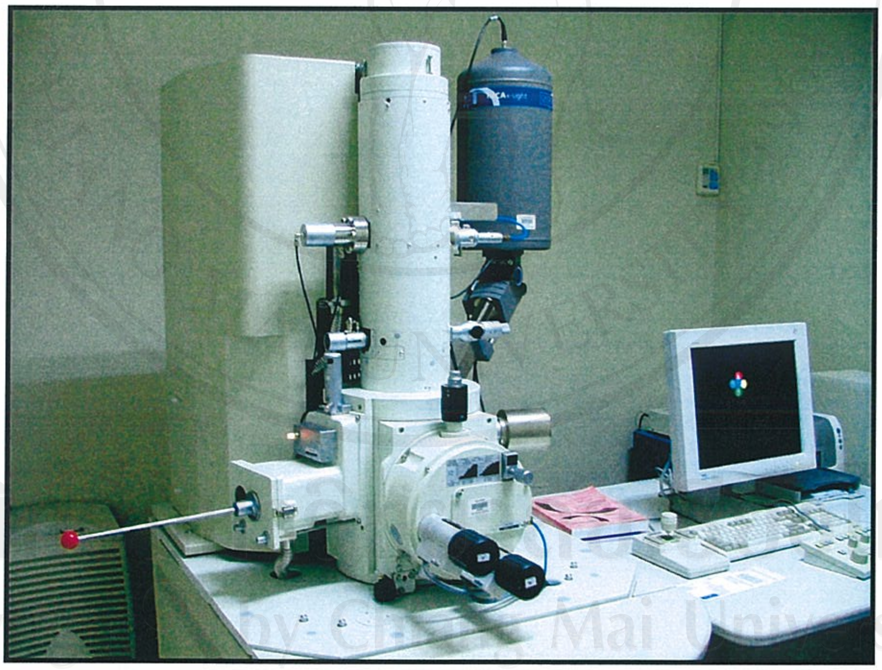

Fig. 3.8 Scanning electron microscope.

3.2.4 Densification analysis

In this study, the bulk densities of sintered ceramics were determined by a method based on the Archimedes principle. It is often more helpful to use the percentage of theoretical density, i.e. the relative density (ρ_r) of the ceramics, which was determined by dividing the measured bulk density (ρ_b) by the theoretical density (ρ_{th}):

$$\rho_r\,(\%) = \left(\frac{\rho_b}{\rho_{th}}\right) \times 100 \tag{3.5}$$

The theoretical density is the density of a material calculated from the number of atoms per unit cell and the unit cell parameters determined by X-ray diffraction.

By recording dimensions and the weights of the sample before and after sintering, the level of shrinkage and weight losses occurring during sintering may be calculated for each sample using the following equations:

$$Shrinkage\ (\%) = \left(\frac{l_b - l_a}{l_b}\right) \times 100 \tag{3.6}$$

where l_b and l_a are the lengths of the samples before and after sintering, respectively.

$$Weight\ loss\ (\%) = \left(\frac{W_b - W_a}{W_b}\right) \times 100 \tag{3.7}$$

where W_b and W_a are the weights of the samples before and after sintering, respectively.