CHAPTER 3

EXPERIMENTAL PROCEDURES

This chapter describes all the experimental procedures employed in this work to synthesis, fabricate and characterize the desired perovskite materials, with their electrical properties tailored by methods of ceramic nanocomposite approaches.

3.1 Sample Preparation

Fabrications of materials, including (micro/nano) powder preparation and ceramic nanocomposites fabrication have been employed as follow:

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

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Powders	Source	Formula weight	Purity (%)	
PbO	Fluka*	223.189	99.99	
MgO	Fluka*	40.311	99.00	
Nb ₂ O ₅	Aldrich**	265.807	99.99	
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

** Aldrich Chemical Company Inc., USA

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

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 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.

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

3.1.1.1 Preparation of PMN powders

The columbite and corundum method were chosen for preparation of PMN powders. It essentially comprised two mixed oxide reaction stages as follows: in the first stage MgO was reacted with Nb₂O₅ to give MgNb₂O₆ and Mg₄Nb₂O₉ (columbiteand corundum-like phase), and in the second stage, PbO was reacted with the MgNb₂O₆ and Mg₄Nb₂O₉ to give the final product of perovskite PMN. Columbite method:

Stage 1)	$MgO + Nb_2O_5$	\rightarrow	MgNb ₂ O ₆	(3.1)
Stage 2)	$3PbO + M\sigma Nb_2Oc$	_	$3Ph(Mg_{1/2}Nh_{2/2})O_{2}$	(3 2)

Corundum method

Stage 1)
$$4MgO + Nb_2O_5 \rightarrow Mg_4Nb_2O_9$$
 (3.3)

Stage 2)
$$12PbO + Mg_4Nb_2O_9 + 3Nb_2O_5 \rightarrow 12Pb(Mg_{1/3}Nb_{2/3})O_3$$
 (3.4)

The starting powders of PbO, MgO and Nb₂O₅ were used, and the mixing process described in 3.1.1 was followed. Conditions for optimizing the calcinations were carefully determined. A schematic diagram of the powder preparation route for MgNb₂O₆ and Mg₄Nb₂O₉ and PMN powders is illustrated in Fig. 3.2



Fig. 3.2 Two-stage mixed oxide processing route to perovskite PMN powders.

3.1.1.2 Preparation of PT powders

Lead titanate powders were prepared by 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 dioxide (TiO₂) as follows:

$$PbO + TiO_2 \rightarrow PbTiO_3$$
 (3.5)

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



Fig. 3.3 Mixed oxide synthetic route to PT powders.

3.1.1.3 Preparation of PMN-PT powders

(a) PT Nanopowders

Lead titanate nanopowders were prepared by using a simple mixed oxide synthetic route. Instead of employing a ball-milling procedure, use was made of a rapid vibro-mill (McCrone Micronizing Mill). The milling operation was carried out in ethanol inert to the polypropylene jar. Various milling times ranging from 0.5 to 30 h were selected in order to investigate the phase formation characteristic of lead titanate and the smallest particle size. After drying at 120 °C, conditions for optimizing the calcination were carefully determined.



Fig. 3.4 Flow chart for preparation of PT nanopowders.

(b) PMN/PT powders

PMN powder (from section 3.1.1.1) and PT nanopowder (from section 3.1.1.3 *(a)*) were selected for preparing PMN/PT powders. The compositions of (1-x)PMN-xPT ($0.1 \le x \le 0.5$) were set for fabricate PMN/PT ceramic nanocomposites by using the concept of bimodal particle size (micron sized PMN + nano sized PT powders), whereby the dispersed phase of nanosized PT component cannot has a higher

concentration than its matrix phase counterpart. In the mixing process, the calculated relevant proportions of constituents were weighed, suspended in ethanol and intimately mixed in a vibro-mill with alumina 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.) and the dried powder was then ground into the fine powders (Fig. 3.5).



Fig. 3.5 Flow chart for the preparation of PMN/PT powders.

3.1.2 Ceramic fabrication

All ceramic fabrication was carried out by adding 3wt% polyvinyl alcohol (PVA) binder, prior to pressing as pellets in a pseudo-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, taking care not to touch the pellet. The specimen arrangement diagram is shown in Fig. 3.6. Alumina crucible was closed with an alumina lid before insertion into a high temperature sintering furnace.

3.1.2.1 Fabrication of PMN ceramics

Sintering was carried out with a dwell-time of 2 h at each step, with constant heating rates of 5 °C/min applied [136] (Fig. 3.7). Variation of the firing temperature between 1100 °C and 1250 °C was carried out for the single-stage sintering samples. Four sets of the first sintering temperature (T_1) were investigated for the two-stage sintering case: 950 °C, 1000 °C, 1050 °C and 1100 °C. Variation of the second sintering temperature (T_2) between 1100 °C and 1250 °C was carried out for each case.



Fig. 3.6 Sample arrangement for the sintering process.

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Fig. 3.7 Preparation of PMN ceramics employing a two-stage sintering method.

3.1.2.2 Fabrication of PT ceramics

Sintering was carried out with a dwell-time of 2 h at each step, with constant heating rates of 1 °C/min applied [81] (Fig. 3.8). Variation of the firing temperature between 1150 °C and 1250 °C was carried out for the single-stage sintering samples. Three sets of the first sintering temperature (T_1) were investigated for the two-stage sintering case: 700 °C, 800 °C and 900 °C. Variation of the second sintering temperature (T_2) between 1000 °C and 1250 °C was carried out for each case.



Fig. 3.8 Preparation of PT ceramics employing a two-stage sintering method.

3.1.2.3 Fabrication of PMN-PT ceramic nanocomposites

Each (1-*x*)PMN-*x*PT powders (from section 3.1.1.3 (*b*)) was mixed with approximately 3 wt% PVA binder, pressed into 15 mm diameter pellets by pseudouniaxial pressing and sintered at temperature between 1100 °C and 1250 °C for 2 h at a heating rate of 5 °C/min. In order to reduce loss of volatile components e.g. lead, the samples were surrounded with the atmosphere powder of identical chemical composition (Fig. 3.6).

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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

3.2.1.1 TG and DTA

Weight loss and thermal decomposition behavior of the uncalcined powders was analyzed by thermogravimetric analysis (TG) and differential thermal analysis (DTA). In this experiment, Perkin Elmer TGA7 (Fig. 3.9) and Perkin Elmer DTA7 (Fig. 3.10) were employed with platinum crucibles, reference powder of Al_2O_3 and a heating rate of 10 °C/min. The weight loss and decomposition temperature were recorded when the samples were heated from room temperature to 1350 °C.



Fig. 3.9 Thermogravimetric analysis (Perkin Elmer TGA7).



Fig. 3.10 Differential thermal analysis (Perkin Elmer DTA7).

3.2.1.2 Thermal expansion

The ceramic samples were cut in the bar shapes (5 mm long and 1 mm thick). Each sample was placed inside a fused silica holder and the thermal expansion was measured as a function of temperature using a linear voltage-differential transformer (LVDT) dilatometer with full automatic temperature control and data collection, shown in Fig. 3.11. The sample was heated at a rate of 2 °C/min from -150 °C up to about 550 °C. The LVDT has an advantage over the other transformer, it gives a linear output for every unit displacement.

Thermal expansion, x_i can be calculated using the equation:

$$x_i(T) = \frac{\Delta l(T)}{l_0}$$
(3.6)

where l_0 is the dimension of the sample at ambient temperature and Δl is the different of the dimension before and after measuring. The thermal expansion coefficient, α_i :

$$\alpha_i(T) = \frac{\Delta x_i(T)}{\Delta T}$$
(3.7)

where Δx is the difference of thermal expansion and ΔT is the difference of the temperature between the two recorded strains

On analyzing the deviation of the strain from the high-temperature linear behavior, P_d values can be obtained at various temperatures. From the phenomenological approach we know that the P_s values can be extracted by using the relation [137];

$$x_{ij} = \frac{\Delta l}{l} = Q_{ijkk} P_k^2 \tag{3.8}$$

where x_{ij} is the strain, $\Delta l/l$ is thermal expansion, Q_{ijkk} is the electrostrictive coefficient. Q coefficients are determined in paraelectric phase (in this work, $Q_{ijkk} = Q_h = Q_{11} + 2Q_{12}$) and considered constant and P_k is the polarization.



Fig. 3.11 Push-Rod LVDT dilatometer system (Model 7/24DCDT-250, Hewlett-Packard).

3.2.2 Phase analysis

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. 3.12) was employed. Lattice parameters of the materials were determined from XRD data.

The amount of the major phase presents in each sample, in principle, was estimated using the following equation as suggested by Swartz and Shrout [28], on the basis of relative intensities of the major reflections for the major and minor phases:

Major phase (wt%) =
$$\left(\frac{I_{Major}}{I_{Major} + I_{Minor}}\right) \times 100$$
 (3.9)

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_{Major} refers to the intensity of the highest major peak and I_{Minor} to the intensity of the highest minor (e.g. Pb₃Nb₄O₁₃ or PbTi₃O₇) 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 [4,8]. The average particle size and lattice strain were also estimated from XRD patterns (the highest intensity peak) using Scherrer equations [138]

$$B = \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2$$

 $2t\sin\theta_1 = (m+1)\lambda$ $2t\sin\theta_2 = (m-1)\lambda$ $t(\sin\theta_1 - \sin\theta_2) = \lambda$

But θ_1 and θ_2 are both very nearly equal to θ_B , so that

$$\theta_1 + \theta_2 = 2\theta_{\rm E}$$

and

$$\sin(\frac{\theta_1-\theta_2}{2}) = (\frac{\theta_1-\theta_2}{2})$$

Therefore

$$2t(\frac{\theta_1 - \theta_2}{2})\cos\theta_{\rm B} = \lambda$$

$$=\frac{0.9\lambda}{B\cos\theta_{P}}$$

t:

(3.10)

where t is diameter of crystal particle,

 λ is X-ray wavelength (1.54 Å),

B is the full-width at half maximum (FWHM) (radians) and

 $\cos \theta_B$ is an angle of reflection.

For lattice strain determination, the following equation was used [138]:



(3.11)

where *b* is lattice strain.

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Fig. 3.12 X-ray diffractometer (Model: Siemens D-500).

3.2.3 Particle size distribution analysis

The particle size distributions of the powders were determined by laser diffraction technique (DIAS 1640 laser diffraction spectrometer) (Fig. 3.13). The powders were dispersed in water and deposited in a container. These samples can be determined in range of 0.04-500 μ m. During determination, the powders were dispersed with stirrer speed of 20 rpm.

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Fig. 3.13 Laser diffraction spectrometer (Model: DIAS 1640).

3.2.4 Densification analysis

The densities of all samples were determined using the Archimedes' method. The sample is first weighed dry (W_1) , then weighed again after fluid impregnation (W_2) , and finally weighed while being immersed in water (W_3) . Then the density value (ρ) can be calculated from the following equation [139]:

$$\rho_C = \left(\frac{W_1}{W_2 - W_3}\right) \times \rho_{H_2O} \tag{3.12}$$

where ρ_{H_2O} is the density of water (in g/cm³), which is slightly temperature

dependent.

The theoretical density can be found from JCPDS files of the materials. For relative density can be calculated from the following equation:

Relative density =
$$\frac{\rho}{\text{Theoretical density}}$$
 (3.13)

The fired shrinkages (and weight loss) of all sintered samples were measured from the percentage diameter (and weight) change (Δl and Δw) with respect to the original diameter (l_o) (and weight, w_o) before sintering [140].

Shrinkage (%) =
$$(\frac{\Delta l}{l}) \times 100$$
 (3.14)

Weight loss (%) =
$$(\frac{\Delta W}{M}) \times 100$$
 (3.15)

3.2.5 Morphological and microstructural analysis

3.2.5.1 Scanning electron microscopy (SEM)

In this work, A JEOL JSM-840A (Fig. 3.14) was used to determine the morphology of the powders and microstructure of the ceramics. The powders were dispersed in an ethanol using ultrasonic cleaner, and then coated with gold sputtering. For ceramics, the samples were cleaned by ultrasonic cleaner and coated with gold. 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). Powder

mophologies and particle sizes were directly estimated from the SEM micrographs. Average grain size of the sintered ceramics were estimated by using linear intercept method [141], where random lines were drawn on a micrograph and the number of grain boundaries intercepting these lines counted.



Fig. 3.14 Scanning electron microscope (Model: JEOL JSM-840A).

3.2.5.2 Transmission electron microscopy (TEM)

A transmission electron microscopy (TEM) was employed to investigate the morphology and chemical homogeneity of the key powders. Samples for TEM were prepared by grinding, dispersed in ethanol and deposited by pipette on to 3 mm holey copper grids for observation by TEM (CM30, Philips, Eindhoven, The Netherlands) (Fig. 3.15) operated at a 200 kV accelerating voltage. In addition, attempt was made to evaluate the crystal structures of the observed compositions/phase by correcting the XRD and TEM diffraction data with the crystallography softwares (e.g. CaRine 3.0).



Fig. 3.15 Transmission electron microscope (Model: CM30, Philips).

3.2.6 Electrical analysis

3.2.6.1 Dielectric measurement

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 - 100 kHz and temperature range of -150 °C to +180 °C for PMN and PMN-PT ceramic-nanocomposites. When higher temperature measurements were requested, a high temperature measurement cell (NorECS Probastat) was used, as shown in Fig. 3.16. Prior to the measurements, the surfaces of the samples were polished with 3 μ m Al₂O₃ 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 ±3 °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 100 kHz PMN and PMN-PT ceramic-nanocomposites and 1 - 5 MHz for PT ceramics. The diameter of the samples was at least 10 times the thickness to avoid fringing field effects. The dielectric constant (ε_r) was calculated by the following Eq. 3.15:

$$\varepsilon_{\rm r} = \frac{Cd}{\varepsilon_0 A} \tag{3.16}$$

where C is the capacitance (Farad), ε_o is the permittivity of free space (8.854×10⁻² F/m), and A and d are the electrode area and thickness of the sample in meters, respectively.



Fig. 3.16 The sample holders for dielectric measurement at: (a) low temperature (-150 °C to 100 °C) and (b) high temperature (25 °C to 1000 °C).

3.2.6.2 Ferroelectric measurement

Polarization measurements were performed using an RT66A ferroelectric test system (Radiant Technologies) in virtual ground mode (Fig. 3.16). The RT66A Standardized Ferroelectric Test System is specifically designed to perform the test required for characterizing non-linear ferroelectric thin film 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 μ m Al₂O₃. They were cleaned with detergent, 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. 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.



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