CHAPTER 3

EXPERIMENTAL TECHNIQUES

In this chapter, the detailed description of the various experimental techniques used, including sample preparation for barium stannate titanate $Ba(Ti_{0.9}Sn_{0.1})O_3$: BTS10 with B_2O_3 are presented. The principles and measurement techniques such as x-ray diffraction (XRD), scanning electron microscope (SEM) and electrical measurements are also investigated and analyzed.

3.1 Sample Preparation

The present BTS10 ceramics with B_2O_3 were prepared by a conventional ceramics method. All commercial starting powders which were used for the preparation of the compositions in this study are listed in Table 3.1, along with the suppliers, formula weight and purities. The schematic diagram of fabrication process for BTS10 with B_2O_3 addition is shown in Figure. 3.1.

Table 3. 1 Specifications of the starting powders used in this study.

Powder	Source	Formula Weight	Purity (%)
$BaCO_3$	Fluka, Switzerland	197.37	$\geq$ 98.5
TiO_2	Fluka, Switzerland	79.87	99-100.5
SnO_2	Riedel de Haen, France	150.71	> 99.8
B_2O_3	Sigma-Aldrich, USA	69.62	98.0

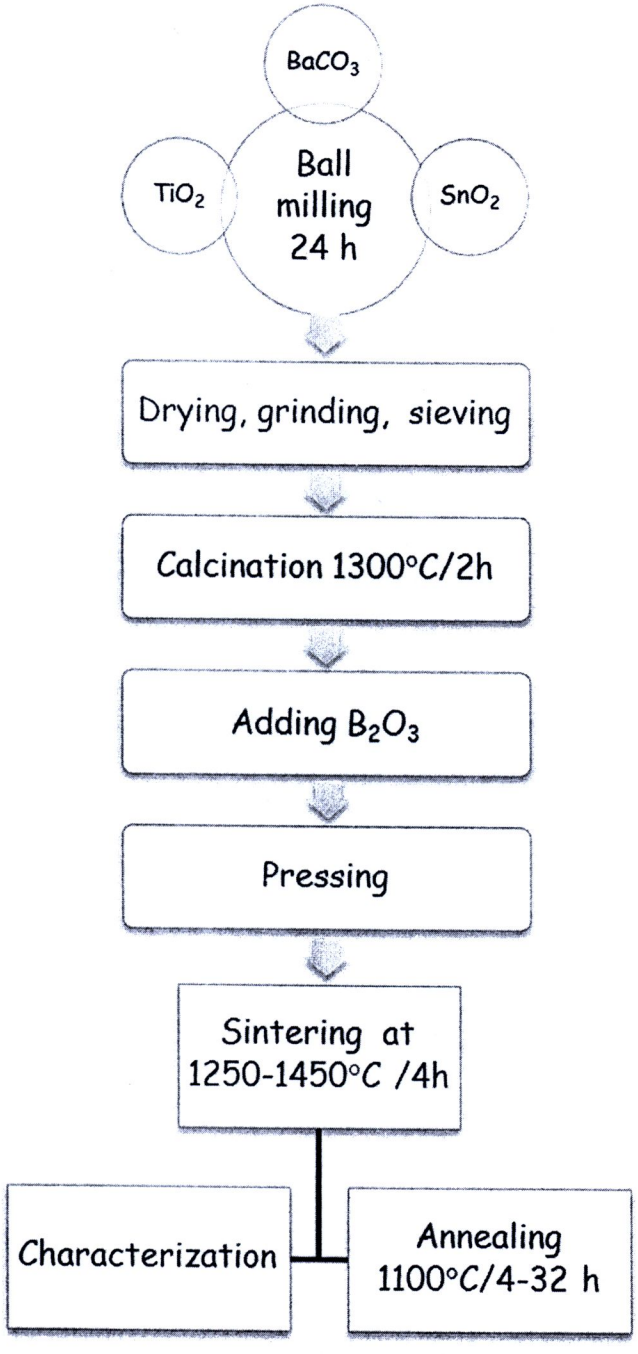

Figure 3. 1 Schematic diagram of the experimental procedure of BTS10 sample.

The powders of $BaCO_3$, TiO_2 and SnO_2 were first weighted according to the stoichiometry of $Ba(Sn_{0.1}Ti_{0.9})O_3$, then mixed and ball milled in an ethanol medium (Merck, Australia) for 24 h, using ZrO_2 balls as grinding media. The slurry was slowly dried by heating at 80°C on a hot plate with continuous stirring (IKA RH basic 2, Malaysia) in action to prevent gravitational separation of the components. The dried powder was then ground by an agate mortar and sieved to separate the particle size. The fine powder was calcined in closed alumina crucible at 1300°C for 2 h. The various amounts of B_2O_3 (0, 1, 2 and 3 wt. %) were added to the calcined powder by ball milling. The obtained powders were mixed with 3 wt.% of polyvinyl alcohol (Fluka, Switzerland) as a binder and then pressed into a disc-shaped pellet of 15 mm diameter under the pressure of 80 MPa. The pellets were subsequently sintered in an electric furnace (Lenton, UK) at 1250-1450 °C for 4 h using a heating/cooling rate of 5°C/min.

3.2 Sample Characterization

3.2.1 The x-ray diffraction technique (XRD)[1]

In order to study phase formation of the samples, XRD is used to identify the crystallographic phases of powders and pellets. The X-rays will give the diffraction patterns that reveal the crystallographic structure of the materials. Constructive interferences of the diffracted X-rays are obtained at angles that follow the Bragg's Law:

$$n\lambda = 2dsin\theta \tag{3.1}$$

where n is the order of diffraction (integer), λ is the wavelength of the incident beam, d is the interplanar spacing of crystal plane, and θ is the angle between incident beam and the particular crystal plane. In this study, the X-ray diffractometer (Bruker A8 Diffractometer, Germany) was performed at room temperature. The incident beam used as X-rays source is CuKα with wavelength of 1.541 Å. The diffractometer was operated at 40 kV and 20 mA. The scanning was done at 2θ angle between 10-110 ° with a step-size of 0.05° per second throughout the measurement period. An X-pert high score plus program was used to determine and interpret the phase formation.

3.2.2 Densification analysis[2]

In this study, the bulk density and apparent porosity of the sintered samples were measured by the Archimedes method using distilled water as the fluid medium. Before the measurement, the specimens were dried to constant mass, W_d, afterward boiled in distilled water for 5 h and then soaked for an additional 24 h. After impregnation of the test specimens, they were suspended in water and determined the weight as W_{sus}. The specimens were blot with a moistened cotton cloth to remove excess water from the surface and weighed immediately to saturated mass, W_{sat}, after the determination of the suspended mass. Calculate the bulk density (ρ_{bulk}) as follows:

$$\rho_{bulk} = \frac{W_d}{W_{sat} - W_{sus}} \times \rho_w \tag{3.2}$$

where ρ_w is the density of water which is temperature dependent,

$$\rho_w = 1.0017\text{-}0.0002315T \tag{3.3}$$

where T is the temperature of water in degree Celsius. Furthermore, the apparent porosity of the samples can be calculated from the equation,

$$Apparent\ porosity\ (\%) = \frac{W_{sat} - W_d}{W_{sat} - W_{sus}} \times 100 \tag{3.4}$$

The linear shrinkages were also measured from the percentage diameter change, Δl, with respect to the original diameter, l_0, before sintering as follows:

$$Linear\ shrinkage\ (\%) = \frac{\Delta l}{l_0} \times 100 \tag{3.5}$$

3.2.3 Scanning electron microscopy (SEM)[3]

SEM is one of the electron microscopy techniques that can be used to image sample surface with high spatial resolutions (<1-20 nm). Nowadays, SEM becomes a highly useful tool in various research fields as it provides a lot of information on the physical, structural, and compositional properties of a wide range of materials with simple sample preparation steps. In SEM, high energy beam of electrons that is generated by an electron gun in the high vacuum electron optical column are focused by condenser lenses and directed toward the sample surface by the objective lenses. The scanning coils deflect the beam horizontally and vertically so that its spot scans in a raster fashion over a square area of the sample surfaces. When they hit the sample, the incident electrons interact with the solid and undergo a successive series of elastic and inelastic scattering events. The elastic scattering of the incident electrons result in the high-energy backscattered electrons, while the inelastic scattering results in the emission of secondary

electrons, Auger electrons, characteristics X-rays. Secondary electrons with energies less than 50 eV can only escape from the material within about 100 Å of the sample surface. They give much better resolution and depth of field as compared to the optical microscopes. The scattered electrons are then collected by the detectors. The detectors convert them to an electrical signal which is subsequently amplified and fed to the grid of display CRT. The amplified image modulates the brightness of the CRT and produces the sample image on viewing screen. The image magnification results from the ratio of the area scanned on the specimen to the area of the display CRT screen. Thus, to increase the magnification in an SEM, the electron beam is scanned over a smaller area of the specimen. The surface morphology and cross-section of ceramics were studied by using a JEOL SEM (JSM 6335FLCZ, Japan). The samples to be studied were coated with a thin layer of gold by using *dc* sputtering machine (BΔL-TEC Sputter Coater SCD005, Switzerland). The gold coating was done to prevent the accumulation of static electric fields due to the electron irradiation during imaging (charging effect) and to improve the image contrast.

3.2.4 Hardness measurement[4]

Hardness (*H*) is ability of material to resist to permanent indentation or penetration. Since it is measuring the contact pressure, hardness can be defined as the ratio of the indentation force over the projected contact area. In this research, the surface hardness of the sintered samples was characterized by a micro hardness tester (Buehler 1600-6100, USA). The Vickers indenter, a conical shape diamond tip with 90° cone angle, was performed under load of 100 N and maintained for 15 s. and ten

positions of indentation were measured different random surface locations in order to obtain average hardness value of samples. Vickers hardness (H_V) measurements were calculated using the following formula:

$$H_V = 1.854 \times \frac{F}{d^2} \tag{3.6}$$

where F is loading force in gf and d is Arithmetic mean of the two diagonals in mm.

3.2.5 Dielectric measurement[5]

To study the dielectric properties, both flat surfaces of the sintered samples were polished and then electroded with a conducting silver paint. The samples with silver paste were fired at 650°C for 15 min to obtain good adhesion to sample surfaces. The dielectric constant (ε_r) and dielectric loss ($\tan\delta$) of the pellet samples were measured in the frequency range of 1 kHz-1 MHz and the temperatures ranging from -20 to 100 °C with a heating and cooling rate of 3°C/min using a compact temperature calibration bath (Hart Scientific 7340, USA), an impedance analyzer (Agilent 4192A, Japan) and a furnace tube in conjunction with a computer-controlled temperature. A measured capacitance value was converted to ε_r, using the following equation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{3.7}$$

where C is the capacitance (F), d is the thickness (m), ε_0 is the dielectric of free space (8.854×10^{-12} Fm^{-1}), and A is the area (m^3) of the samples.

3.2.6 Piezoelectric measurement

Before measurement, an electric field of 1.5 kV/cm was applied using a high voltage (Hipotronics HD100 Series AC/DC Hipot, USA) to a sample which was being immersed in a heated silicon oil (~100°C) to prevent break down voltage. In order to saturate polarization, the poled sample was left for 24 h in air. After that the piezoelectric coefficient (d_{33}) was measured with a d_{33} meter (KCF PM3001, USA). The direct d_{33} value is displayed on a 3-1/2 inch digital meter.

3.2.7 Ferroelectric measurement

Ferroelectric properties of material are typically determined by making electrical measurements using characterization circuits. In this work, the system for performing ferroelectric measurements included a Radiant Precision LC Materials Analyzer (Radiant Technologies, USA), Trek 610D High voltage supply and Radiant Technologies Precision high voltage interface The hysteresis loops of the ceramics were measured by applying an electrical field in the range of 100-1000 kV/cm. The hysteresis period was 1 ms and the pre-loop delay was 1000 ms.

3.2.8 Complex impedance spectroscopy

In this work, the impedance measurement was employed by using an impedance gain phase analyzer (Solartron 1260, USA) which combined with a probe station and a stable temperature fluid chuck systems (Signatone, USA). These systems include a gold plated wafer chuck and a self-contained heater/chiller system that cycles temperature conditioned water through the wafer chuck. The temperature tests

are in the range of 15°C to 300°C. Then, the ZView-2 software was used for analysis the impedance data.

3.3 References

[1] H.P. Klug, L.E. Alexander, X-ray diffraction procedures for polycrystalline and amorphous materials, 2d ed., Wiley, New York, 1974.

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[3] F.C. Kartawidjaja, Heterolayered $Pb(Zr_xTi_{1-x})O_3$ Thin Films, in: Materials Science and Engineering, National University of Singapore, Singapore, 2009.

[4] ASTM E384-11, in: Standard test method for Knoop and Vickers hardness of materials.

[5] D.W. Richerson, Modern ceramic engineering : properties, processing, and use in design, 2nd ed., M. Dekker, New York, 1992.