CHAPTER 2

EXPERIMENTAL

BNT and BLNT powders have been first prepared by solid state reaction of the constituent metal oxides or carbonates.[3-58] However such reactions often lead to compositional and structural inhomogeneities in the powders produced. Moreover, ceramics prepared at high temperatures have a very large particle size, higher impurities content due to repetitive calcination and grinding steps, a lower chemical activity and are not suitable for enhancing the dielectric properties for high performance uses. Precipitation from nitrate solutions[97,98] is one of the chemical processing techniques that can produce fine particle size, a high degree of chemical homogeneity of the powder and reduced calcination temperature of the BNT powder.

The hydrothermal synthesis[99-103] is a convenient technique for the preparation of various multicomponent oxide materials, which have utility in numerous electronic applications. Hydrothermal systems are useful for the precipitation of ceramic powders of fine particle size and uniform morphology in a single experimental step at moderate temperature and pressure. The most commonly used precursors for the hydrothermal synthesis of BNT powders are nitrates, chlorides, oxychlorides, acetates, hydroxides and titanium alkoxides.

The use of catalyst or mineralizer for synthesis of BNT powders is necessary as it increases the solubility of the starting precursors. Concentrations of the catalyst play an important role in the formation of BNT and BLNT powders.

2.1 CHEMICALS

1. Bismuth nitrate, $Bi(NO_3)_3.5H_2O$, assay 98 %, Aldrich , U.S.A.
2. Sodium nitrate, $NaNO_3$, assay 99.5%, Riedel-de Haen, U.S.A.
3. Titanium isopropoxide, $Ti(OC_3H_7)_4$, assay 99%, Aldrich, U.S.A.
4. Lanthanum nitrate, $La(NO_3)_3.3H_2O$, assay 99.9%, Aldrich, U.S.A.
5. Ammonia solution, NH_4OH, assay 25 %, BDH, England
6. Nitric acid, HNO_3, assay 65 %, Merck, Germany
7. Hydrogen peroxide, H_2O_2, assay 30 %, Carlo Erba, Italy
8. Sodium hydroxide, NaOH, assay 99%, Merck, Germany
9. Absolute ethanol, C_2H_5OH, assay 99.0-100.0 %, Merck, Germany

2.2 APPARATUS AND INSTRUMENTS

1. X-ray diffractometer (Siemens, D500), Germany
2. Scanning electron microscope (JEOL, JSM 5410LV), Japan
3. Vernier (Zim-ZEEM), China
4. Furnace (Carbolite, SCF 1200), England
5. Furnace (Thermolyne), England
6. Vacuum oven (VOS-300 SD), Japan

7. Balance (Mettler Toledo AB 304-S), England
8. Particle size analyzer (Malvern Masterizer), England
9. Ultasonic bath (Cole-Parmer, 5880), U.S.A

2.3 EXPERIMENTAL PROCEDURES

2.3.1 Synthesis of BNT powders

2.3.1.1 Preparation of the solution:

The clear solutions of 0.025 M bismuth titanate and 0.025 M sodium nitrate were prepared and mixed together into the teflon-line cup. An aqueous solution of 0.050 M titanium isopropoxide in 6M nitric acid was then added into the mixed solution in the ratio theoretically necessary to obtain the desired $Bi_{0.5}Na_{0.5}TiO_3$, and NaOH at various concentrations was used as the mineralizer for adjusting pH of the final solution.

2.3.1.2 Hydrothermal process:

Hydrothermal synthesis of the BNT powders was performed under autogeneous pressure in a 500 ml teflon-line cup autoclave. The synthesis temperature varied from 150 to 200 °C, the mineralized concentration ranged from 10-12 M NaOH, and the holding periods ranged from 5 to 45 hours. The total volume of the solution should be below 125 ml which produces an autogeneous pressure up to 0.6 MPa. After cooling down, the solid portion was separated from the extracted suspensions by filtration. The product was washed with deionized water until a pH of the final solution reached 10. The wet powders were dried in an oven at 100 °C for 5

hours. Figure 2.1 shows the flow chart for the synthesis BNT powders by hydrothermal process.

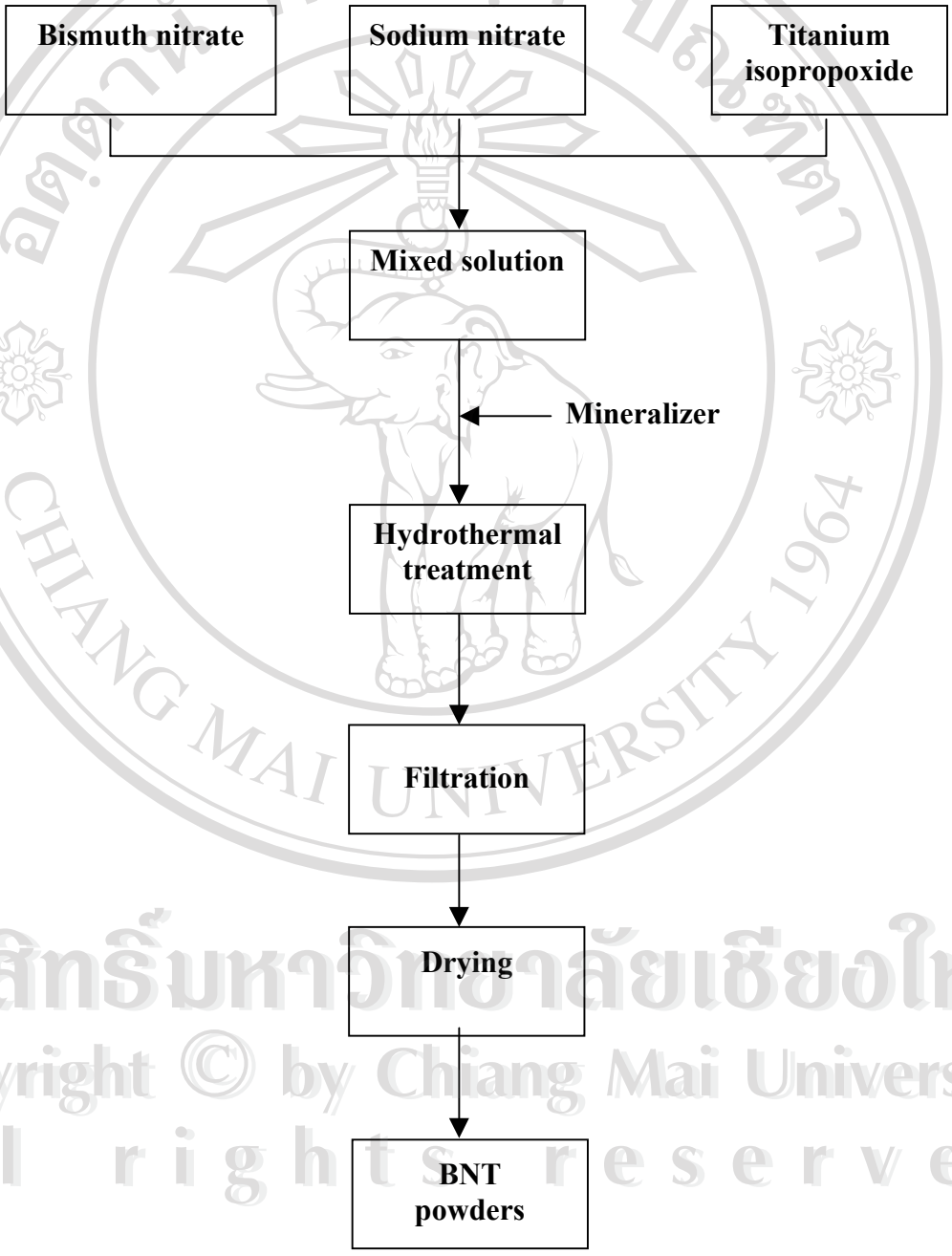

Figure 2.1 Schematic diagram for the synthesis of BNT powders by the hydrothermal process.

2.3.2 Synthesis of BLNT powders

2.3.2.1 Hydrothermal process

Clear aqueous solutions of 0.025 M bismuth titanate and 0.025 M sodium nitrate were prepared. Lanthanum nitrate, at 1-6 mole % lanthanum, was added into the mixed solution and mixed together into the teflon-line cup. An aqueous solution of 0.050 M titanium isopropoxide in 6M nitric acid was then added into the mixed solution in the ratio theoretically necessary to obtain the desired $(Bi_{0.5}Na_{0.5})_{(1-1.5X)}La_xTiO_3$, and NaOH at various concentrations was used as the mineralizer for adjusting the pH of the final solution. The same procedure used to prepare BNT powders by the hydrothermal process was used to synthesize BLNT powders. The synthesis temperature was 200 °C with holding period of 20 hours. Figure 2.2 shows the flow chart for the synthesis BLNT powders by hydrothermal process.

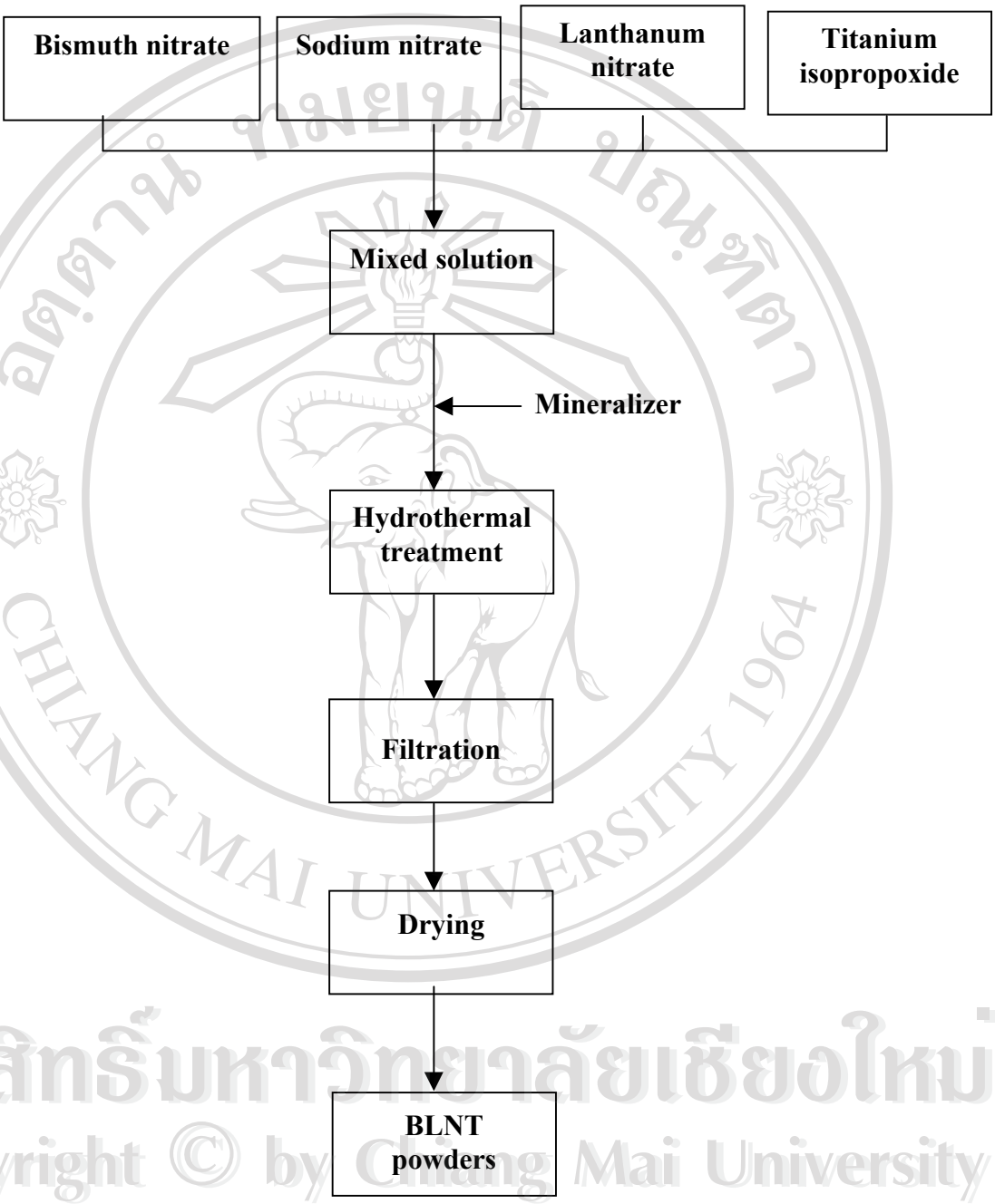

Figure 2.2 Schematic diagram for the synthesis of BLNT powders by the hydrothermal process.

2.4 POWDERS CHARACTERIZATION

2.4.1 X-ray Diffraction (XRD)

The crystalline structure and phase transformation of BNT powders were studied by X-ray diffraction.

Sample preparation

Crystallographic and phase analyses were performed on an X-ray diffractometer (Siemens, D 500) operating at 25 kV and 20 mA, using CuK_{α} radiation. The detection range of 2θ values was 20° to 60° with scan step increments of 0.1°. Identification of crystalline phases was carried out by comparison of XRD patterns with JCPDS standards.

2.4.2 Scanning Electron Microscopy (SEM)

The particle size, morphology and microstructure of BNT powders were investigated using scanning electron microscopy.

Sample preparation

The particle size, morphology and microstructure of BNT powders were characterized by scanning electron microscope (JEOL, JSM 5410LV). The powders sample were dispersed in absolute ethanol using ultrasonic bath. The suspension was dropped on gold conductive tape attached to the surface of the SEM brass stub. The stub was then coated with palladium-gold by plasma sputtering for 2 minutes, and an accelerating voltage of 20 kV was used.

2.4.3 Particle Size Distribution Analysis

The particle size distribution was measured using a particle size analyzer.

Sample preparation

The particle size distribution was measured using a particle size analyzer (Malvern Masterizer S219), with a detection limit above 0.1 μm. The samples were prepared by dispersing the BNT powders in deionized water using a high intensity ultrasonic probe. Both the differential and cumulative particle size distributions were calculated in terms of the number and volume percentage.

2.5 CERAMICS CHARACTERIZATION

2.5.1 Ceramics preparation

BNT and BLNT powders were pressed in a 2 cm cylindrical die, the pressure applied was 10 MPa. The green pellets were placed in an alumina crucible. The specimens were embedded in a BNT bed and also surrounded in BNT powders, which was used for the Bi_2O_3 atmosphere buffer. Sintering was carried out in a furnace under air atmosphere using a heating and cooling rate of 10 °C/min. The sintering temperature was varied from 800 °C to 1000 °C at different holding periods of 1-3 hours.

2.5.2 X-ray Diffraction (XRD)

The phase present after sintering was identified on a X-ray diffractometer (D 500) operating at 25 kV and 20 mA, using CuK_{α} radiation. The detection range of 2θ values was 20° to 60° with scan step increments of 0.1°.

2.5.3 Scanning Electron Microscopy (SEM)

The sintered microstructure of BNT and BLNT ceramics were studied by scanning electron microscopy. (JEOL JSM 5410LV).

2.5.4 Measurement of density

The density of sintered pellets was measured by an immersion technique and calculated using Archimides principle. A dry sample was weighed and then submerged in the hot distilled water for 2 hours, to ensure that all-open porosity within the pellets were filled. The saturated pellets were first weighed in the room temperature distilled water and weighed again in the air using a wire basket. Density of the pellets can be calculated by the following formula:

$$\text{Density} = \frac{Wt_{(dry)}\, D_{(liq)}}{Wt_{(sat)} - Wt_{(susp)}}$$

Where $Wt_{(dry)}$ is the weight of the dry pellets,

$Wt_{(sat)}$ is the weight of the saturated sample weighing in air,

$Wt_{(susp)}$ is the weight of the sample weighing in distilled water,

$D_{(liq)}$ is the density of the water at the experiment temperature.