CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Chemical Reagents

All of raw materials are reagent grade chemical

1. $BaCO_3$ 99% of purity by Fluka
2. TiO_2 99% of purity by Reidel
3. MgO 99% of purity by Fluka
4. Nb_2O_5 99.99% of purity by Aldrich
5. Bi_2O_3 99% of purity by Reidel
6. Li_2CO_3 99% of purity by Reidel
7. PbO 99.99% of purity by Merck
8. silver paste and acetone
9. absolutely ethanol 99.99% of purity by Merck

3.2 Synthesis Processing

The synthesis processing was separated in 2 procedures.

3.2.1 Powders and ceramics preparation of $x\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}(1\text{-}x)\text{BaTiO}_3$ binary system (where $0 \leq x \leq 0.07$) were produced by different 2 mixed oxide method as following below:

Firstly, mixing the various ratios of all oxide powders (as $BaCO_3$, TiO_2, MgO and Nb_2O_5) together on the same time and calcined at 1200 °C for 2 hours in air, this processing was called P1. The flow chart can be shown in Figure 3.1.

Secondly, the mixture of $BaCO_3$ and TiO_2 powders were calcined at 1200 °C for 2 hours in air to produce BT powder and the mixture of $BaCO_3$, MgO and Nb_2O_5 powders were calcined at 1200 °C for 2 hours in air to produce BMN powder. After that various ratios of BT and BMN powders were mixed and calcined at 1200 °C for 2 hours in air, this processing was called P2. The flow chart can be shown in Figure 3.1.

The chemical powders were weighed and then ball milled with zirconia balls in ethyl alcohol for 24 hours and died in an oven (at about 100 °C). PVA 2 weight percent solution was used to be binder. The powders were pressed into disc shape by uniaxial pressing at 60 MPa to produce the green pellets have the diameter about 1.5cm. The green compact samples were sintered at various temperatures between 1300 °C to1500 °C for 2 hours in air. They were heated by controlling the furnace temperature at the rate 5 °C/min. All of compositions were shown in TABLE 3.1.

TABLE 3.1 Sample composition of additive-BMN in weight percent.

P1: Processing				Chemical Composition	**P2**: Processing	
Nb_2O_5(g)	MgO(g)	TiO_2(g)	$BaCO_3$(g)	x	BT(g)	BMN(g)
0.38	0.06	33.88	84.54	0.01	98.91	1.09
0.76	0.12	33.50	84.46	0.02	97.81	2.19
1.14	0.17	33.13	84.38	0.03	96.72	3.28
1.51	0.23	32.76	84.30	0.04	95.64	4.36
1.89	0.29	32.39	84.22	0.05	94.55	5.45
2.27	0.34	32.01	84.14	0.06	93.47	6.53
2.647	0.40	31.64	84.06	0.07	92.39	7.61

n.b. Sample compositions are of the form xBa($Mg_{1/3}Nb_{2/3}$)O_3-(1-x)$BaTiO_3$ and prepare for total weight about 100 g.

3.2.2 Powders and ceramics preparation of 0.02Ba($Mg_{1/3}Nb_{2/3}$)O_3-0.98$BaTiO_3$ (From P1 processing) binary system with low melting point additives as Bi_2O_3, Li_2CO_3 and PbO, this processing was called S1 and S2. The optimum conditions from 3.2.1 were used to be the precursor powder for this procedure. Mixtures of powder Bi_2O_3, Li_2CO_3 and PbO were then blended with the precursor powder according to the sample compositions shown in TABLE 3.2. The powder samples were ball milled once more in ethyl alcohol for 24 hours, dried and pressed to from disc-type pellets under 60 MPa pressure. The obtained green compact samples

were then sintered at various temperatures between 800 °C to 1000 °C for 2 hours in air. They were heated by controlling the furnace temperature at 5 °C/min. The flow chart can be shown in Figure 3.2.

TABLE 3.2 Sample compositions with sintering additives in weight percent.

Processes	Code	Sample Compositions		
		0.02BMN-0.98BT (g) from P1 processing	Bi_2O_3/Li_2CO_3 (g) x	PbO (g) y
S1	A	99	1	-
	B	98	2	-
	C	97	3	-
	D	96	4	-
	E	95	5	-
	F	94	6	-
	G	90	10	-
S2	Sample A	98.25	1.32	0.43
	Sample B	96.50	2.63	0.87
	Sample C	92.99	5.26	1.75

n.b. Sample compositions are of the form $(100\text{-}x\text{-}y)$ $[0.02Ba(Mg_{1/3}Nb_{2/3})O_3\text{-}0.98BaTiO_3]\text{-}xBi_2O_3/Li_2CO_3\text{-}yPbO$ and prepare for total weight about 100 g.

Bi_2O_3/Li_2CO_3 indicated that the equivalent mole of Bi_2O_3 and Li_2CO_3.

3.3 Linear Shrinkage and Density Measurements

3.3.1 Linear Shrinkage Measurement

$$\text{Percentage of linear shrinkage} = \frac{\Delta L}{L_O} \times 100 \qquad 3.1$$

where $L_0 = 1.5$ cm (block diameter)

$$\Delta L = L_0 - L_s$$

3.3.2 Density Measurement

The method of measuring the density of a piece of ceramic material usually described in standards is based on the Archimedes principle. This principle states that the weight of an object in a fluid equals its by weight minus the buoyant force (or the weight of the fluid displaced). However, it is usual to measure open porosity levels at the same time by ensuring that during immersion liquid can penetrate all parts of the specimen through the open porosity. Typical procedures are;

1. Dry specimen(s) in air at 100 °C, store in a desiccators, weigh when cold (mass W_1)
2. Boil in distilled water for a period, typically 1 hour.
3. Weigh immersed in water (W_2).
4. Remove, lightly dab the surface with a damp cloth to remove surface moisture without drying the interior, and reweigh (W_3). This step is tricky and requires some practice but can be reasonably reliable.
5. Repeat procedure to check on constancy of weightings, particularly W_3, if necessary.

6. Calculations;

$$\text{Bulk density (g/cm}^3) = \frac{W1}{W_3 - W_2} \times \rho_{st} \qquad 3.2$$

Where, ρ_{st} is the density of water at the temperature of weighting.

3.3 Characterisation

A. Phase Identification

Phase analysis of powders and ceramics were carried out by XRD technique to identify crystal structure, phase formation and contamination of impurities as second phase and precursor materials. XRD result showed the set of d-spacing to obtain from material. This analysis was carried out based on the Joint Committee on Powder Diffraction Standard (JCPDS). Data collection was performed in the 2θ range of 20°-60° with a step size of 0.02° and counting time of 2 sec per step. The relative amounts of perovskite and second phase were approximated by calculating the ratio of the major XRD peak intensities of the perovskite and second phase via the following equation:

$$\text{Perovskite intensity (\%)} = \left(\frac{I_{perovskite}}{I_{perovskite} + I_{second\ phase}} \right) \times 100 \qquad 3.3$$

Moreover, the samples were analyzed by scanning electron microscopy (SEM), back scattering (BSE), energy dispersive X-ray (EDX) to confirm and support the data from XRD.

B. Electrical Measurements

The samples were polished to be parallel plate. Silver paste was applied on both faces of the sample disc for electrical measurements. Evolution of the

dielectric constant against the temperature was measured at various ambient temperatures ranging from room temperature 25 °C to around 150 °C at 1 kHz. Using a LCZ meter (Hewlett Packard 4276A and Hewlett Packard 4284A). And the resistivity was measured at room temperature by High Resistance Meter (Hewlett Packard 4339B).

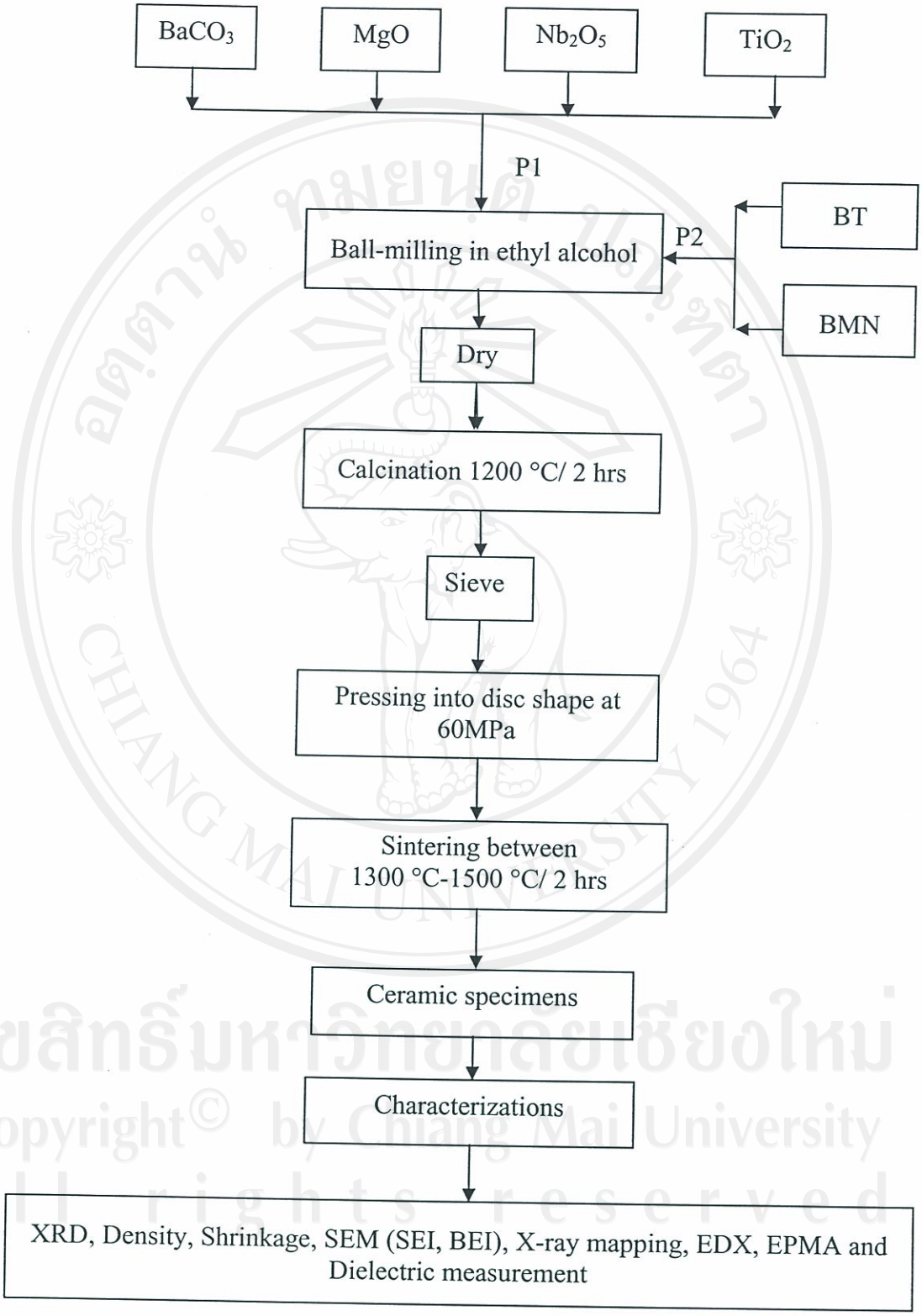

Figure 3.1 Show the flow chart diagram of P1 and P2 processing.

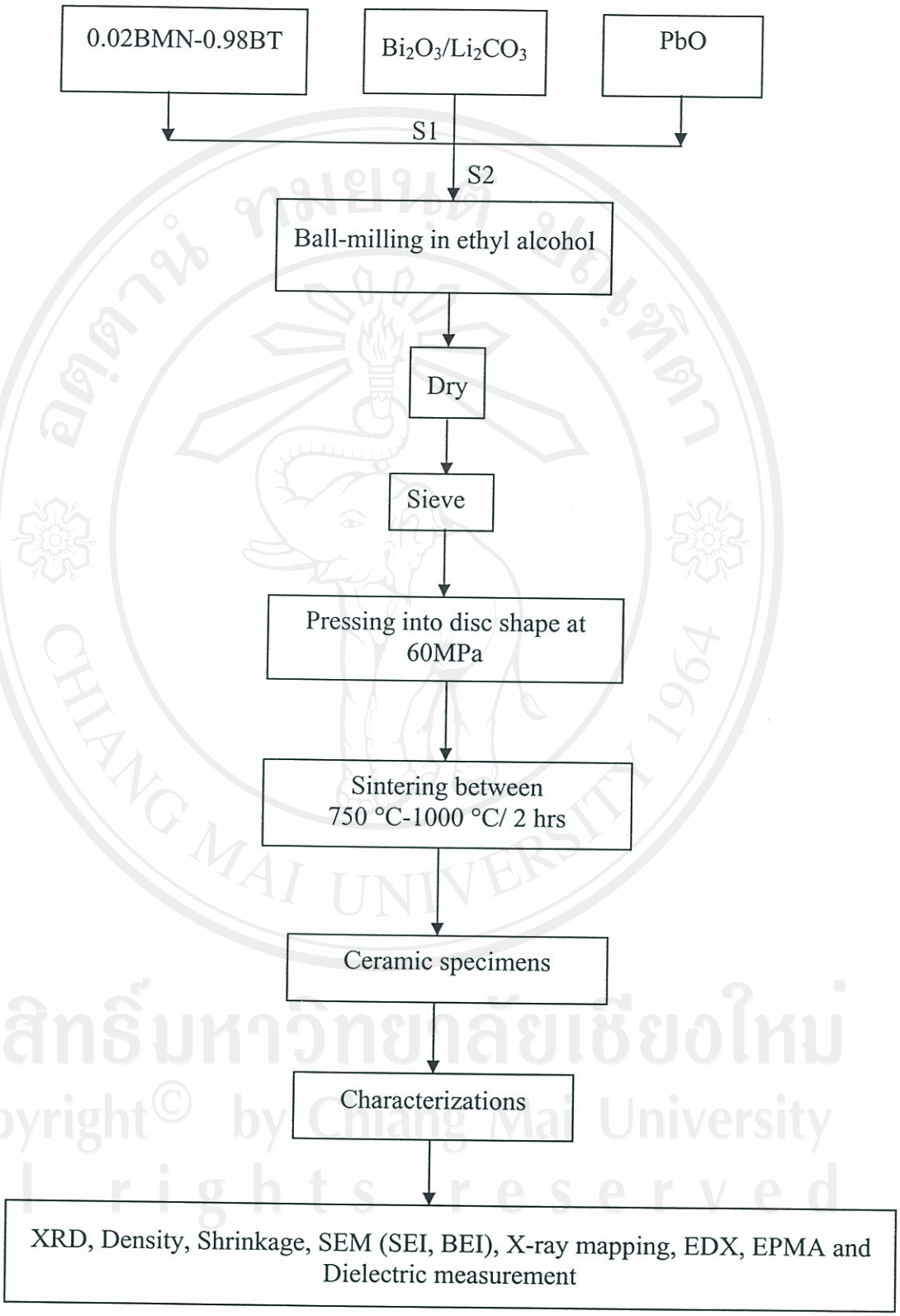

Figure 3.2 Show the flow chart diagram of S1 and S2 processing.