CHAPTER III

MATERIALS AND METHOD

In this chapter, the experimental procedures employed for preparation and characterization of BNT-BKT-based ceramics are described. The ternary system piezoelectric ceramics of (1-x-y)$(Bi_{0.5}Na_{0.5})TiO_3$-x$(Bi_{0.5}K_{0.5})TiO_3$-y$BiFeO_3$, (1-x-y)$(Bi_{0.5}Na_{0.5})TiO_3$-x$(Bi_{0.5}K_{0.5})TiO_3$-y$Bi_{0.5}Li_{0.5}TiO_3$ and (1-x-y)$(Bi_{0.5}Na_{0.5})TiO_3$-x$(Bi_{0.5}K_{0.5})TiO_3$-y$K_{0.5}Na_{0.5}NbO_3$with$0.12 \leq x \leq 0.24$ fixed $y=0.03$; $0 \leq y \leq 0.07$ fixed $x=0.18$, $0.18 \leq x \leq 0.26$ fixed $y=0.10$; $0 \leq y \leq 0.12$ fixed $x=0.20$ and $18 \leq x \leq 0.28$ fixed $y=0.03$; $0 \leq y \leq 0.07$ fixed $x = 0.20$, respectively (abbreviated as BNKFT-x/y, BNKNT-x/y and BNKLT-x/y, respectively) are prepared in this work. The details are presented in the following sections.

Sample Preparation

Fabrications of materials, including powder preparation and ceramics fabrication have been described as follow:

Preparation of BNKFT, BNKLT and BNKNT powders

The ternary system BNKFT, BNKLT and BNNKT were synthesized by combustion method. Reagent grade Bi_2O_3, $NaCO_3$, TiO_2, Fe_2O_3, K_2CO_3, Li_2CO_3 and Nb_2O_5 were used as starting materials. The details of these oxides; such as the supplier, formula weights and purities, are listed in Table 5. First, these oxides or carbonate powders were weighed in appropriate stoichiometry. The ball-milling technique was employed for the mixing and milling in this work. The powders were mixed by ball milling for 24 h. with ethanol as a solution media. Drying was carried out on a hotplate with a magnetic stirring until the mixture nearly dry, and then placed in a 120 °C drying oven for 2 h. The suspensions were dried and the powders were ground using an agate mortar and then sieved into a fine powder. The mixed powders and glycine ($C_2H_5NO_2$) were mixed with a ratio of 1:2 in an agate mortar. The BNKFT, BNKNT and BNKLT powders were then calcined at various temperatures until the optimum condition was determined.The calcined powders were

analyzed by X-ray diffraction technique to determine the amount of the perovskite phase percentage.

Table 5 Specifications of starting materials used in this study

Materials	Source	Formula weight	Purity (%)
Bi_2O_3	Qrec	208.98	99.5%
$NaCO_3$	Riedel-de Haën	22.99	99.5%
TiO_2	Sigma-Aldrich	47.90	99.5%
Fe_2O_3	Riedel-de Haën	55.85	97.0%
K_2CO_3	Riedel-de Haën	39.10	98.0%
Li_2CO_3	Merck	6.94	99.5%
Nb_2O_5	Eleps	92.91	>99.95%

Preparation of BNKFT, BNKNT and BNKLT ceramics

The calcined powders received from the processes described in previous sections were mixed with 3 wt.% polyvinyl alcohol (PVA, Fluka) which was used as binder. The mixed powders were pressed by uniaxial hydraulic press to form disc-shaped pellets 10 mm in diameter. Binder was burned out on sintering step at temperature 500 °C for 1 h. The green pellets were placed on the alumina powders-bed inside alumina crucible, before insertion into a high temperature furnace.

Sample Characterization

All powders and ceramics were characterized using different tools as described below in Figure 29.

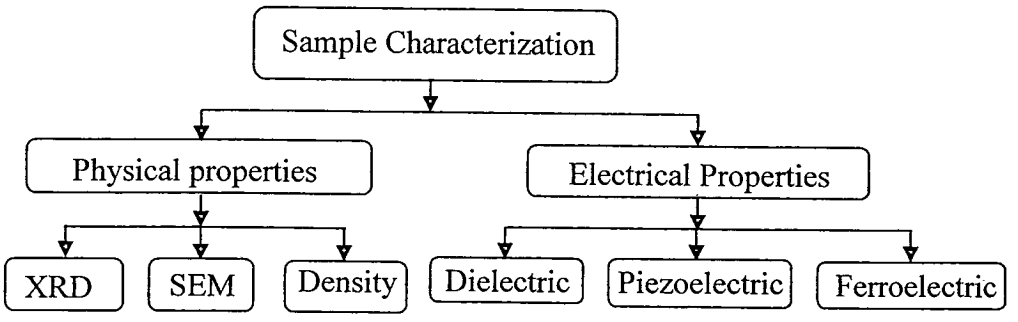

Figure 29 Diagram of experimental procedure on sample characterization

Physical properties

X-ray diffraction (XRD) Technique

The X-ray diffraction (XRD) was used to analyze phase formation and phase purity which was especially important in minimizing pyrochlore phase formation in BNT-BKT based powders and pellets. The room temperature XRD patterns were recorded with a Siemens-D500 diffractometer at Naresuan University with Cu Kαradiation at 20 kV. The relative amounts of the perovskite and pyrochlore phases were estimated from these major peak intensities (110) or the respectively phases. The estimation was suggested by Swartz and Shrout [85] using the following equation:

$$\%\ perovskite\ phase = \left(\frac{I_{perov}}{I_{perov} + I_{Pyr}} \right) \times 100 \qquad (6)$$

This well-known equation is widely employed in connection with the preparation of complex perovskite structure materials.I_{perov}referred to the intensity of the (110) perovskite peak, intensities of the highest, I_{pyr}peaks.

Scanning Electron Microscopy (SEM)

Microstructural characterization of sample surface using scanning electron microscopy (SEM) was performed to determine the grain size and the presence of porosity. Average grain size of the sintered ceramics were estimated by using a linear intercepting method [86,87], where random lines were drawn on a micrograph and the number of grain boundaries intercepting these lines were then counted.

Densification Measurement

The method of measuring the density of a piece of ceramics material usually described in standards is based on the Archimedes principle [87]. This principle stated the weight of an object in a fluid equals it's 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 110 C, store in a desiccator, weigh when cold (mass W_1)

2. Boil in distilled water for a period, typically 3 hoursand leave it for 1 night

3. Weigh immersed in water (W_2) and then weight during immersion liquid can penetrate all parts of the specimen through the open porosity (W_3).

4. Calculate follow this equation:

$$\rho_c = \frac{W_1 \rho_w}{W_3 - W_2} \tag{7}$$

where, ρ_w is the density of water at room temperature (g/cm^3) and is the density of sample at room temperature (g/cm^3); however the density of water is slightly temperature dependent

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

Electrical properties

I. Dielectric Measurement

The dielectric properties of the sintered ceramics were studied as functions of both temperature and frequency with an automated dielectric measurement system. The computer-controlled dielectric measurement system consists of a precision LCR-meter (Agilent 4263B), a temperature chamber, and a computer system. The capacitance and the dielectric loss tangent are determined over the temperature range of 50 and 500 °C with difference frequency.

The dielectric constant was calculated by equation,

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A} \tag{8}$$

Where ε_r and ε_0 are the dielectric constant and permittivity of free space. C is thecapacitance, and t and Aare the thickness and area of the sample.

II. P-E and S-Eproperties measurement

P-E and S-Emeasurements were made using high voltage amplifier (Trek), precision High Voltage Interface (HVI, Radiant Technologies), precision LC (Radiant Technologies) and computerized control and data acquisition. The sample is placed in a High Voltage Test Fixture chamber (HVTF) chamber in bottom half of the fixture. A copper electrode fixed in the bottom of the chamber contacts the electrode on the bottom of the sample. The bottom chamber is sealed so it may be filled with insulating oil to protect the sample from the arcing that may occur in open air. The system is an automated device intended for measuring the polarization of materials induced by a single triangle wave. It can prevent the excess voltage and current during a sample breakdown from exceeding the current canceling capability of the virtual ground circuitry on the tester input. During the measurement, an electric field of 10-60 kV/cm based on the coercive field was applied to a sample which immersed in a silicone oil to prevent the breakdown of the sample

The high field d_{33}* was calculated as the ratio of the maximum strain to the maximum field in the cycle, according to this equation,

$$d_{33}^* = \frac{S_{max}}{E_{max}} \tag{9}$$

where S_{max} and E_{max} are maximum strain and maximum field in the cycle

3. Piezoelectric properties measurement

The optimum poling conditions were determined by poling the ceramics with applying DC field of 5 kV/mm in a stirred oil bath at 120°C for a time period 30 minutes. The piezoelectric constant (d_{33}) was measured using a quasi-static piezoelectric d_{33} meter. The piezoelectric constant (d_{33}) measurements were made directly after poling and after 24 hours. Measurements were conducted at a drive frequency of 100 Hz.