

CHAPTER III EXPERIMENTAL

3.1 Materials

Glacial acetic acid, chloroform, tetrahydrofuran, and diethyl ether were purchased from Carlo. Paraformaldehyde (98.7%) and phenol (99.3%) were purchased from Merck. Methyl alcohol and sodium hydroxide were purchased from Lab Scan. Strontium acetate hydrate (99.995%), ethylenediamine (>99.9%) were purchased from Fluka. Barium acetate, titanium tetra-n-butoxide (97%) and poly (methyl methacrylate-co-ethyl acrylate) were purchased from Aldrich. All of the chemical used for synthesis were analytical grade, and no further purification was performed before use.

3.2 Equipments

3.2.1 Fourier Transformation Infrared Spectroscopy (FTIR)

Functional groups of materials were measured by a fourier transformation infrared spectrophotometer (NEXUS 670 FTIR). The spectra were collected in absorbance mode, the wave number range of 4000-400 cm^{-1} and 32 scans per resolution.

3.2.2 Differential Scanning Calorimeter (DSC)

A heating profile of benzoxazine was performed by a differential scanning calorimeter, DSC 7 (Perkin Elmer) under N_2 purge at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The temperature and heating flow calibration were performed with indium.

3.2.3 Thermo Gravimetric – Dynamic Temperature Analysis (TG-DTA)

Thermal stability and decomposition temperature of polybenzoxazine and composites were performed by a high resolution TG-DTA Pyris Diamond (Perkin Elmer). Samples were loaded on a platinum pan. The mass change with increasing temperature was monitored and recorded from 50 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 flow.

3.2.4 Scanning Electron Microscope (SEM)

Microstructures of sol-gel $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ powders and $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics and filler distribution in the composites were observed by a scanning electron microscope (SEM; JSM-5200, JEOL and JSM-6480LV, JEOL) at voltage of 15 kV. The specimens for SEM were prepared by placing on stub with carbon tape. Each specimen was coated with gold sputtering for 4 minutes before the observation under SEM.

3.2.5 Transmission Electron Microscope (TEM)

The particle size of sol-gel $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ powders was observed by transmission electron microscope (TEM; JEM-2100, JEOL). The powders were dispersed in solvent followed by ultrasonication in order to broken agglomerate powders. Then, they were drop on copper grid and dried before observation.

3.2.6 X-ray Diffraction (XRD)

A crystal phase and structure of sol-gel $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ powders and $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics were analyzed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered $\text{CuK}\alpha$ radiation operated at 40 kV and 30 mA with scan speed 5.00 deg/min from the 2θ range of 5.00 to 90.00 degree.

3.2.7 Pycnometer

The apparent density of sol-gel $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ powders, polybenzoxazine, and composites were measured by pycnometer (Quantachrome, Ultrapycnometer 1000) under helium purge at pressure of 20 psi.

3.2.8 Impedance/Gain-Phase Analyzer

Dielectric properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics and composites were measured by impedance/gain-phase analyzer (Hewlett Packard., model 4194A) in parallel capacitance (C_p) mode, with frequency from 1 kHz to 10 MHz at room temperature. The specimens were prepared by coating gold as an electrode on both sides of the specimens. Before electroding, the major faces of the specimens were polished parallel with silicon carbide powders size of 13 and 5 μm /water slurry respectively, and geometries were recorded. The dielectric constant of materials was calculated from the capacitance by using the following equation:

$$K = \frac{Cd}{\epsilon_0 A}$$

where C is the capacitance (F), ϵ_0 the free space dielectric constant value (8.85×10^{-12} F/m), A the capacitor area (m^2), and d the thickness of specimens.

3.2.9 Ferroelectric Measurement Test System

The polarization and electric field characteristics (Hysteresis loop) were measured by RT66A: standardized ferroelectric measurement test system. Voltage was applied to the specimens, which were immersed in silicone oil at room temperature to observed hysteresis loops.

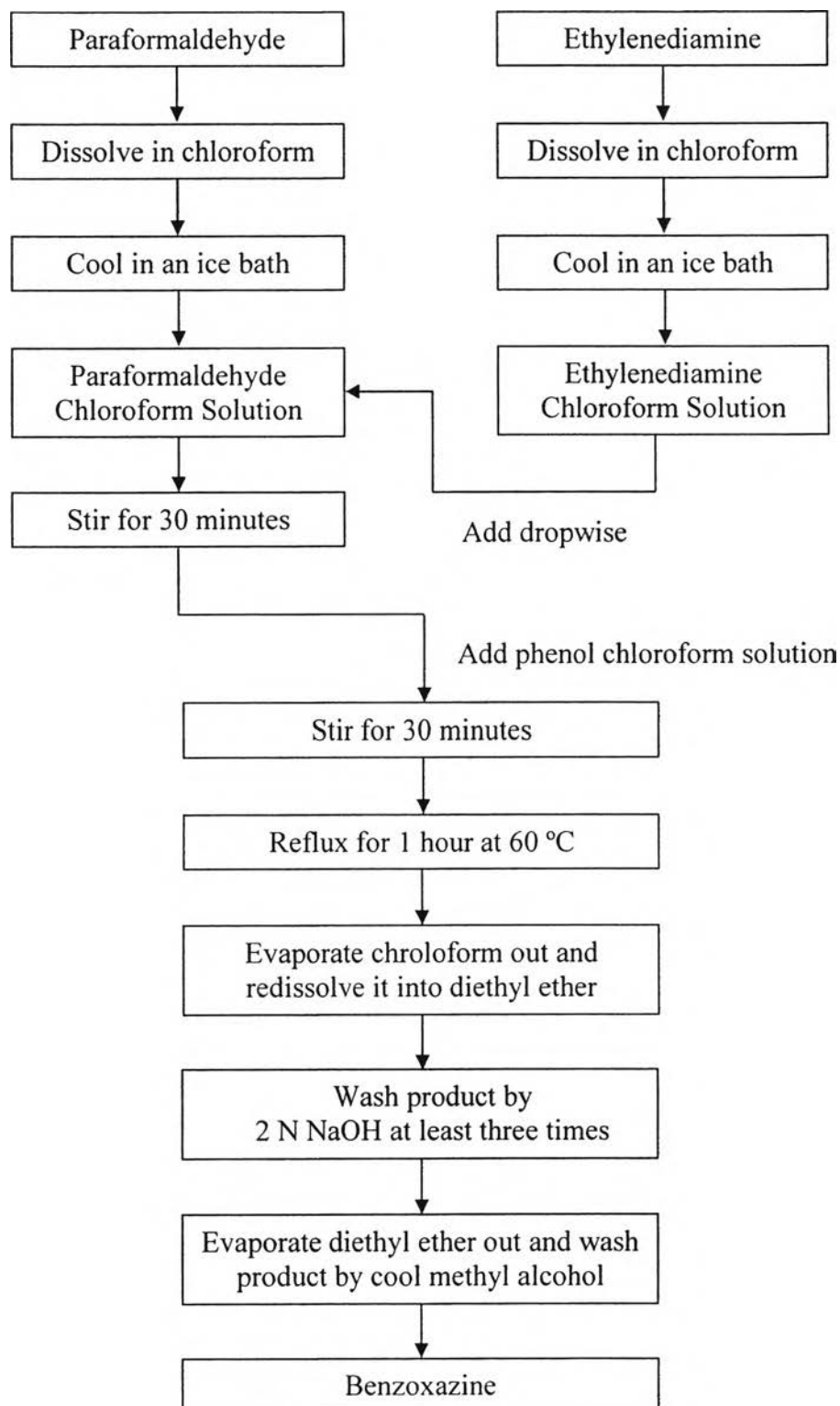
3.2.10 Compression Molding Machine

Polybenzoxazine and composite samples were preformed by a compression press (Wabash, model V50H-18-CX)

3.3 Methodology

3.3.1 Synthesis of Benzoxazine

The synthesis of benzoxazine is based on the reaction of phenol, paraformaldehyde, and ethylenediamine at the molar ratio of 2:4:1 respectively. Solution of paraformaldehyde and ethylenediamine in chloroform was stirred for 30 min in ice bath. Phenol chloroform solution was then added and stirred for 30 min. The mixture was refluxed at temperature of 60 °C for 1 h followed by evaporating chloroform out. To help remove possible unreacted materials from synthesis, purification of the reaction product was carried out. High yellow viscous solution, resulting from synthesis, was dissolved in diethyl ether. The ether solution was washed by 2N NaOH solution in separatory funnel. The ether was then removed with a rotary evaporator. The solid products were washed by cool methyl alcohol through a filter. Washing was repeated at least three times to obtain white benzoxazine powder.



Schematic 3.1 Benzoxazine preparation.

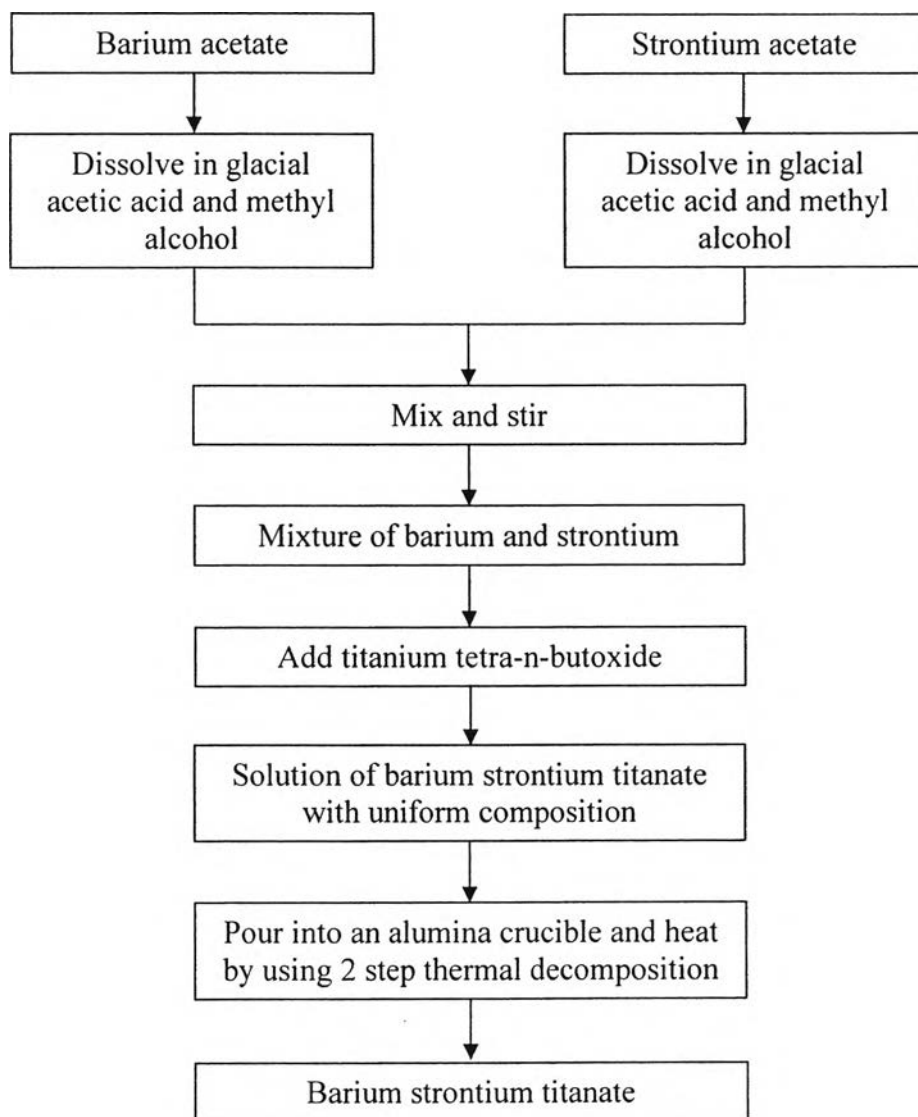
3.3.2 Barium Titanate/Barium Strontium Titanate Preparation

3.3.2.1 *Sol-Gel Process of Barium Strontium Titanate*

For the preparation of precursor solution, barium acetate, strontium acetate and titanium (iv) butoxide were used as the precursor materials. Glacial acetic acid and methyl alcohol were used as the solvents. Barium acetate and strontium acetate were taken in the ratio of 100:0, 70:30, 50:50 and 30:70, then dissolved in heat acetic acid with stirring to obtain clear solution followed by adding methyl alcohol with glacial acetic acid: methyl alcohol ($R_{ac/me}$) of 1:2. Then the equimolar amounts of titanium (iv) n-butoxide was added into this mixture under vigorous stirring. The clear solution was relatively stable and became a gel in a few days at room temperature. The gel is formed by controlled hydrolysis and subsequent polymerization and condensation reaction to form 3-dimensional network of viscous gel. The precursor gel was converted to a dried gel by heating in vacuum oven. The dried gel was calcined by using 2-step thermal decomposition in air in order to decompose the solvent and crystallize the $Ba_{1-x}Sr_xTiO_3$, as shown in Figure. 3.1.

3.3.2.2 *Ceramic Pellet Preparation*

Small amount of poly (methyl methacrylate-co-ethyl acrylate) (binder) was dissolved in acetone. After that, the sol-gel $Ba_{1-x}Sr_xTiO_3$ powders were mixed with binder until a homogeneous slurry material was obtained. Then this slurry material was left overnight under air, followed by grinding and sieving. These powders were then pressed into pellet shape by using a force of 10 tons for 10 mins. The sintering process was performed by putting $Ba_{1-x}Sr_xTiO_3$ pressed disks into the furnace by using the following temperature program as shown in Figure 3.2. The temperature increases from room temperature to 300 °C with heating rate of 2.1 °C/h and hold for 2 h. Then, the temperature increases to 550 °C with the heating rate 2.1 °C/h and hold for 5 h in order to remove binder completely. Afterward, the samples were sintered at 1350 °C for 2 h with heating rate of 4.5 °C/h from 550 °C. After sintering, the samples were cooled to room temperature at the rate of 1.7 °C/h.



Schematic 3.2 Barium strontium titanate preparation.

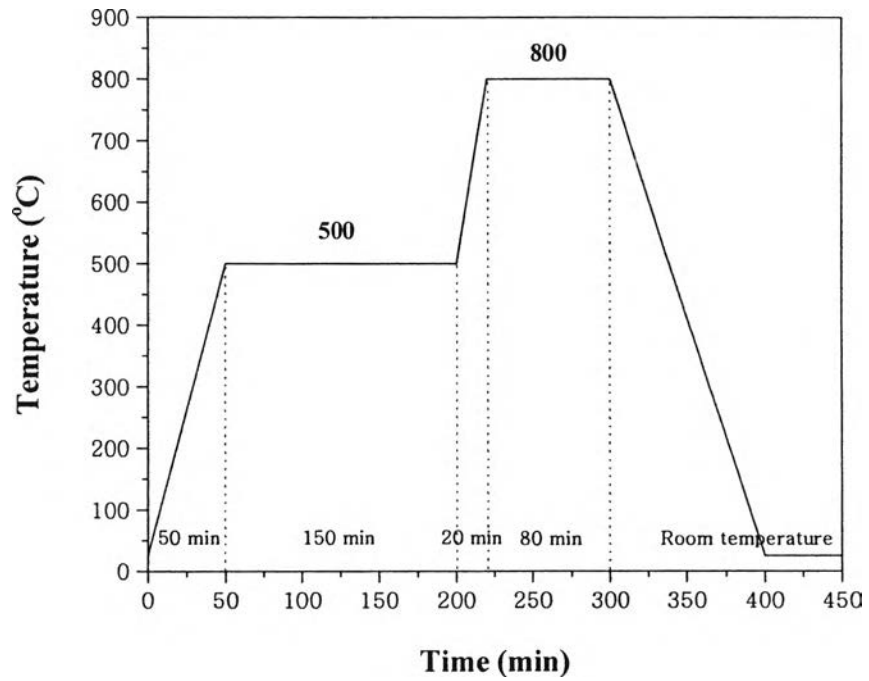


Figure 3.1 Temperature program for the 2-step thermal decomposition.

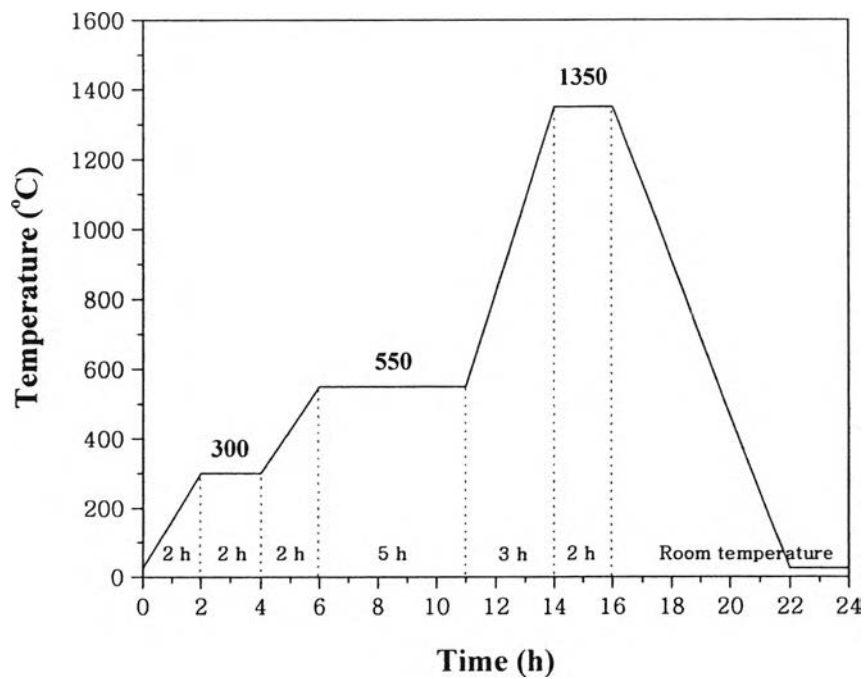


Figure 3.2 Temperature program for the sintering process of ceramic pellet.

3.3.3 Composite Preparation

The polybenzoxazine before curing was in the powder form. Thus the BaTiO₃ and benzoxazine powder could be homogeneously blended by the dry mixing method (mechanically grinding in pestle mortar), with ceramic filler. The composite specimens were prepared by compression molding, and cured at 120 °C for 30 min in order to melt the benzoxazine to flow fill the mold. After that the mold was then closed and the composite was cured at 140 and 160 °C for 30 min, then cured further 1 h at 180 °C under pressure of 10 metric tones (Table 3.1). The disk shape composite specimens of 15 mm diameter and 1 mm diameter were fabricated, and used for further measurements and characterizations.

Table 3.1 Temperature program for compression molding process

Temperature (°C)	Time (mins)	Pressure (10 tons)
120	30	-
140	30	-
160	30	-
180	60	+

- not be compressed

+ compressed by 10 tons