

CHAPTER III EXPERIMENT

3.1 Materials

Glacial acetic acid, methyl alcohol, chloroform, sodiumhydroxide and diethylether were purchased from Italmar. Ethylenediamine (>99.9%) was purchased from ACS Xenon. Paraformaldehyde (98.7%) and phenol (99.3%) were purchased from Merck. Barium acetate was purchased from Lab Scan. Strontium acetate (99.995%) and titanium tetra-n-butoxide (97%) were purchased from S.M. Chemical. All chemicals were used without further purification.

3.2 Equipment

3.2.1 Fourier Transformation Infrared Spectroscopy (FTIR)

Functional groups of the benzoxazine monomers were measured by a Fourier Transformation Infrared Spectrophotometer (FTIR). The measurements were made in absorbance mode using a Bruker FTIR Spectrometer, model Vector 3.0, using 32 scans per resolution.

3.2.2 Gel-permeable Chromatography (GPC)

The molecular weight of the benzoxazine monomers were measured by a gel permeable chromatograph (SHIMADZU class VP) with a Styragel® HT4 7.8x300 mm column containing: Styrenedivirylbenzene-co-polymer and Tetrahydrofuran and a mobile phase containing tetrahydrofuran.

3.2.3 Thermogravimetric Analysis (TGA)

Thermal degradation was performed by a high resolution TG-DTA Pyris Diamond (Perkin Elmer). Samples were loaded on a the platinum pan and heated from 30°C to 800°C with a heating rate of 10°C/min under N₂ flow.

3.2.4 Differential Scanning Calorimeter (DSC7)

A heating profile of benzoxazine monomers were performed by a differential scanning calorimeter 7, DSC 7 (Perkin Elmer) at a heating rate of 10 °C/min. The samples were heated from 30°C to 300°C.

3.2.5 X-ray Diffraction (XRD)

A crystal phase and structure of barium titanate (BT) /barium strontium titanate (BST) were analyzed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered CuK α radiation operated at 40 kV and 30 mA with scan speed 5.00 deg/min from the range of 5.00 to 70.00 deg.

3.2.6 Scanning Electron Microscope (SEM)

Microstructures and surface morphology of BT/BST were performed by a scanning electron microscope (JEOL, model JSM 2590).

3.2.7 Compression Molding Machine

Composite samples were prepared by a compression press (Wabash, model V50H-18-CX).

3.2.8 Transmission Electron Microscope (TEM)

Particle size of barium strontium titanate was measured by a transmission electron microscope TEM 100 keV (JEOL, model MJEM-1230).

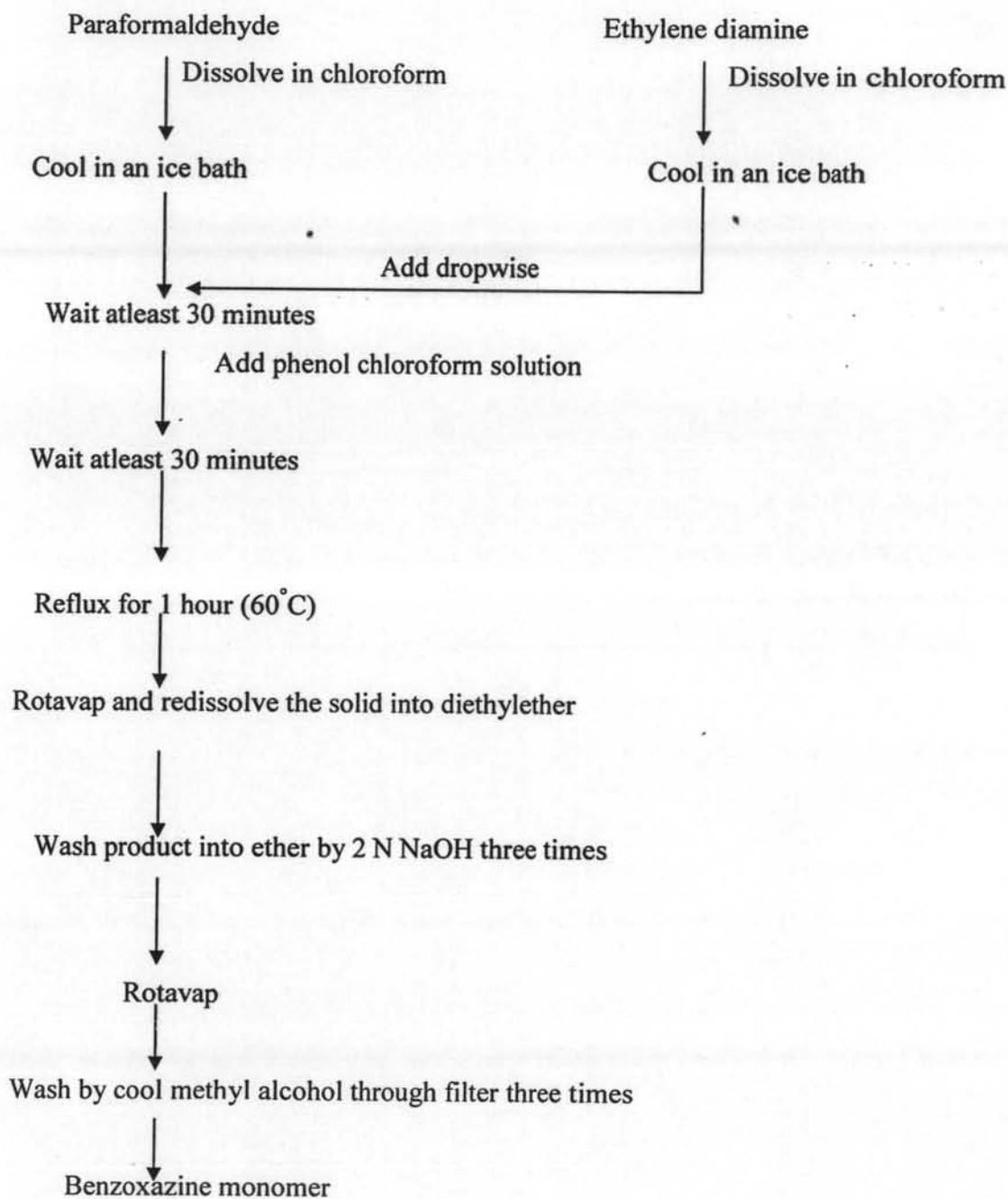
3.2.9 Impedance/Gain-Phase Analyzer

Dielectric constant and loss tangent were measured by impedance/gain-phase analyzer (Hewlett Packard., model 4194A) with frequency from 1 kHz to 1 MHz and temperature from 25°C to 100°C.

3.3 Methodology

3.3.1 Monomer Preparation

Paraformaldehyde and ethylenediamine were separately dissolved in chloroform then both solutions were separately cooled in an ice bath. After that, the ethylenediamine chloroform solution was added dropwise in a paraformaldehyde chloroform solution and stirred for 30 minutes. The phenol chloroform solution was added dropwise into previous mixture and stirred for another 30 minutes. Then, the temperature was increased to reflux temperature (60°C) for 1 hour. The solvent was evaporated by rotavap and redissolved into diethylether. The crude reaction products were washed into ether by 2 N NaOH aqueous solution three times then the solvent was evaporated by rotavap, and the solid products quick washed by cold methyl alcohol through a filter. Washing was repeated at least three times to obtain a benzoxazine monomer.

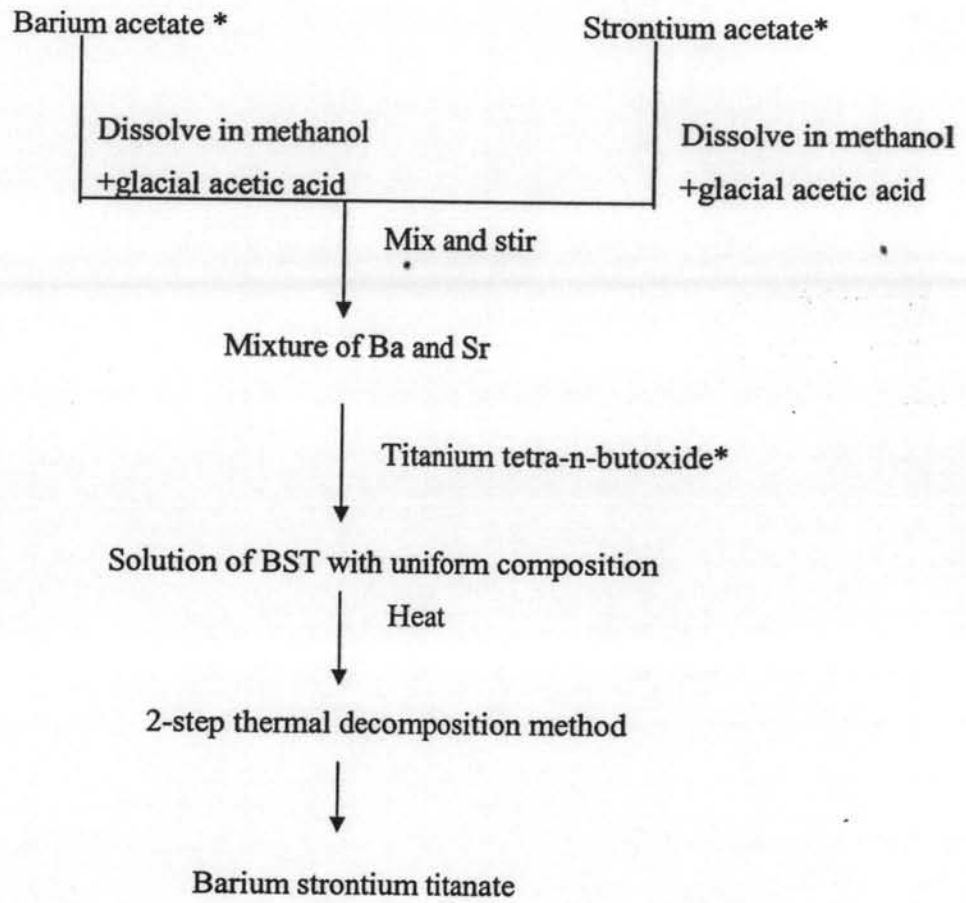


Schematic 3.1 Monomer Preparation.

3.3.2 Barium Strontium Titanate Preparation

3.3.2.1 *Sol-Gel Process of Barium Strontium Titanate*

$(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ was prepared by using $x=0, 0.05, 0.3$ and 0.5 respectively. Equal moles of barium acetate and strontium acetate were dissolved separately into methyl alcohol in the presence of glacial acetic acid. The solutions were then mixed and stirred. The prescribed amount of titanium-n-butoxide was added into the mixture. All the materials mentioned above were thoroughly mixed to prepare a stable solution with uniform composition. After that the solution was poured into an alumina crucible and heated by using a 2-step thermal decomposition method which is shown in Figure 3.1 in order to decompose the precursors and to crystallize the barium strontium titanate. All of materials weighted are summarized in Table 3.1.



Schematic 3.2 Barium Strontium Titanate Preparation.

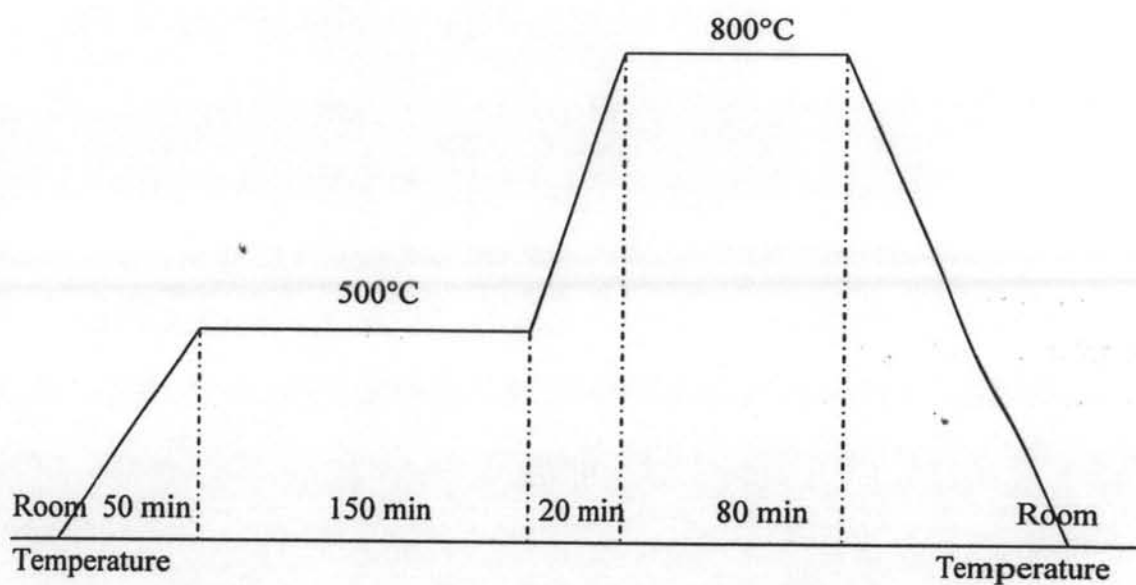


Figure 3.1 Temperature program for the 2-step thermal decomposition method.

Table 3.1 Weight of each chemicals in preparing barium titanate/barium strontium titanate

	Barium acetate	Srontium acetate	Titanium tetra-n-butoxide
BaTiO_3	5.3800g	-	7.20ml
$(\text{Ba}_{0.95}\text{Sr}_{0.05})\text{TiO}_3$	5.1103g	0.2173g	7.20ml
$(\text{Ba}_{0.70}\text{Sr}_{0.30})\text{TiO}_3$	4.4600g	1.5400g	8.52ml
$(\text{Ba}_{0.50}\text{Sr}_{0.50})\text{TiO}_3$	3.1875g	2.575g	8.50ml

3.3.2.2 Ceramic Pellet Preparation

Polyvinyl alcohol (PVA) was weighed (4% by weight of BST powder) then dissolved it into acetone. After that, this solution was poured into sol-gel powders and stirred until a homogeneous slurry material was obtained. Then this slurry material was left overnight under air, followed by grinding and sieving to obtain the powder. Then the powders were pressed in a pellet form by using a force of around 7-8 tons and a sintering process was performed by putting the ceramic pellets into a furnace by using the following temperature program as shown in Figure 3.2. in order to obtain a sintered product for electrical measurement.

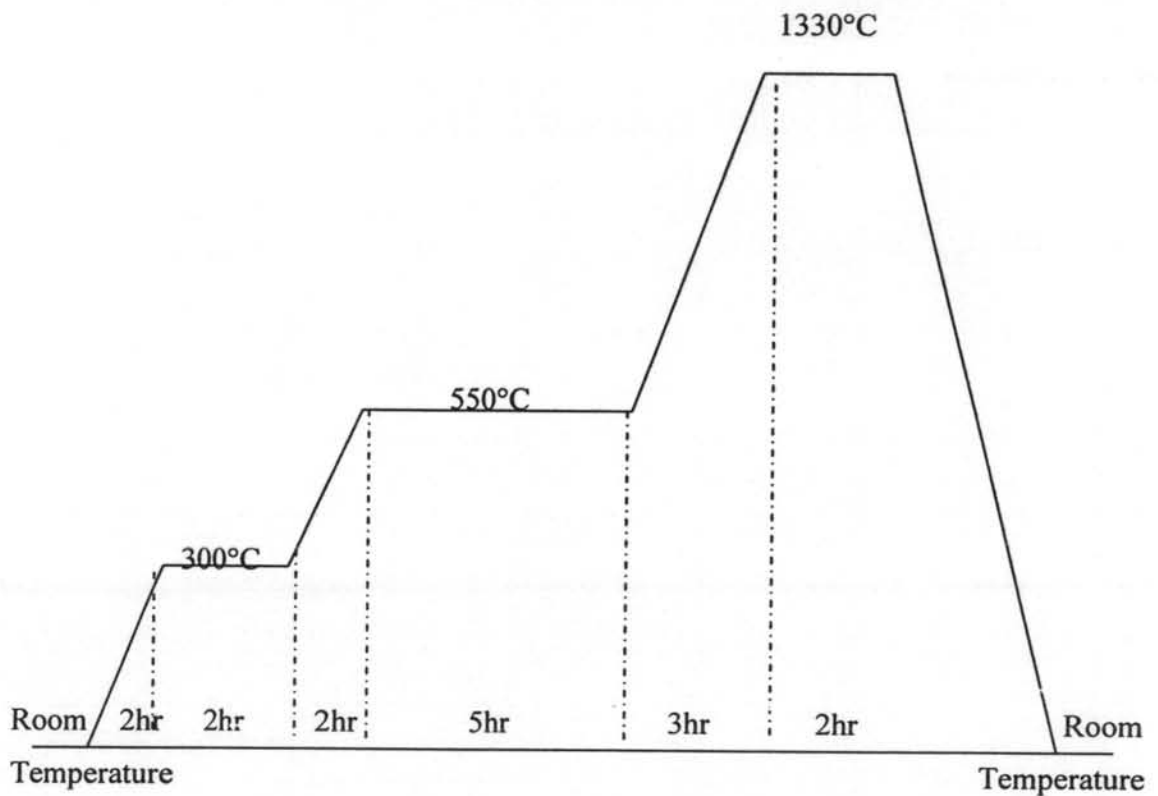


Figure 3.2 Temperature program for the sintering process of ceramic pellet.

3.3.3 Composite Preparation

Benzoxazine monomer and barium strontium titanate were put together and mixed in tumble mixer then they were heated in an oven at 70°C for half an hour to remove any remaining volatiles. The composite was prepared by a Wabash compression press. In the compression molding process, the mold, which measured 17 cm x 13 cm, was first coated with a silicone mold release agent and preheated to 140°C. The mixture of monomer and barium strontium titanate* were put into the preheated mold to fill the mold. The mold was then closed and the composite was cured according to the temperature program shown in Table 3.2

Table 3.2 Temperature program for compression molding process.

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

- not be compressed

+ compressed by 10 tons

*Barium strontium titanate : 1% by wt of composite

5% by wt of composite

3.3.4 Morphology Crystal Structure and Particle Size Determination

Morphology crystal structure of sol-gel and sintered ceramics were measured by SEM 15kV. The sample powders from sol-gel process were dispersed on carbon paper. The fracture and planar surface of sintered sample were placed on carbon tape. All samples were coated with gold before the observation under SEM.

Particle size of sol-gel powders were measured by TEM 100keV. The sample powders were dispersed on carbon-supported copper grids.

3.3.5 Sample Preparation for Dielectric Measurements

Before electroding, the major faces of samples were polished parallel with silicon carbide paper (1000), and geometries were recorded. Then two faces of each samples were coated with gold by ion sputtering device.

Dielectric measurements were carried out at 25°C to 110°C from frequency of 1 kHz to 1 MHz with impedance/grain-phase analyzer. The samples were put between two probes under applied frequencies.