

**CHAPTER II**

**EXPERIMENTAL**

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#### II.1. Materials and Reagents

##### 1-Barium sources

The employed barium sources were barium chloride  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (98.6%, BDH Chemical Ltd) and barium hydroxide  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (Fluka >98%) were used as barium sources.

##### 2-Titanium sources

Titanium dioxide (Fluka >99.8%purity) and titanium isopropoxide (Aldrich 97%) were used as titanium sources.

##### 3-Lead sources

The employed of lead source was lead acetate (99%, Nice Chemical Pvt. Ltd).

##### 4-Organic acids reagents

Oxalic acid, citric acid, tartaric acid, benzoic acid and acetic acid [organic90%, El Nasr Chemical Co.] were used as organic acids reagents.

##### 5-Alkali reagent

The employed alkali source was sodium hydroxide pellets (A.R 98%).

## II.2. Procedure

### II.2.1. *Organic carboxylic acid precursor*

Barium titanate was prepared by dissolving 3.56 gm of barium chloride  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  into 250 ml of deionized water with 1.163 gm of titanium dioxide where the mole ratio of Ba/ Ti equals 1. The amount of titanium dioxide was added step by step with stirring. The mixture was stirred for 15 minute on hot plate magnetic stirrer and the aqueous solution of organic acids added to mixture with stirring. The solution was evaporated to  $80^\circ\text{C}$  with constant stirring until dryness. The dried powders obtained as precursors. The dried precursors formed were calcined at a rate of  $10^\circ\text{C} / \text{min}$  in static air atmosphere up to different temperatures ( $800\text{-}1200^\circ\text{C}$ ) for time period from 0.5- 4 hrs. Table 7 shows the amount of organic acid which added for synthesis of barium titanate. The amount of organic acid was related to stoichiometry ratios of  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  according to the following equations.

For example in case of added oxalic acid, the expected chemical reactions are:



The oxalic acid mole ratio related to both reactions is 1

Table 7: Weight of organic acids used in the synthesis of barium titanate by organic acid precursor

Source of organic acid	Wt of organic acid (gm) at mole ratio 0.5	Wt of organic acid (gm) at mole ratio 1	Wt of organic acid (gm) at mole ratio 1.5
<b>Citric acid</b>	9.15	18.3	27.45
<b>Oxalic acid</b>	5.505	11.01	16.51
<b>Tartaric acid</b>	6.556	13.112	19.668
<b>Benzoic acid</b>	5.33	10.66	15.99
<b>Acetic acid</b>	2.12 ml	5.24ml	7.86 ml

For lead titanate powders, the same procedure was used. Only; we used lead acetate as the source of lead instead of barium chloride. Lead titanate powder was prepared by adding mixture of (7.3228 gm of lead acetate and 1.544 gm of  $TiO_2$ ). The amount of organic acids used was mentioned in Table 8.

Table 8: Weight of organic acids used in the synthesis of lead titanate nanopowders by organic acid precursor

Source of organic acid	Wt. of organic acid (gm) at mole ratio 1
<b>Citric acid</b>	12.18
<b>Oxalic acid</b>	7.301
<b>Tartaric acid</b>	8.617

### II.2.2. Hydrothermal method

Barium titanate nanopowders were prepared by mixing barium hydroxide in deionized water and titanium isopropoxide with stirring at room temperature. The mixture was stirred for 30 min then sodium hydroxide was added to the mixture drop by drop until pH 12-14. Finally, the solution was put into 500 ml autoclave at hydrothermal temperature 180-200°C for hydrothermal time 12-24 hrs. After the reaction processing done the autoclaves were quenched immediately with cold water. The formed precipitate was filtrated and washed with deionized water was dried at 60°C overnight. The schematic diagram of the autoclave used is shown in Fig.14.

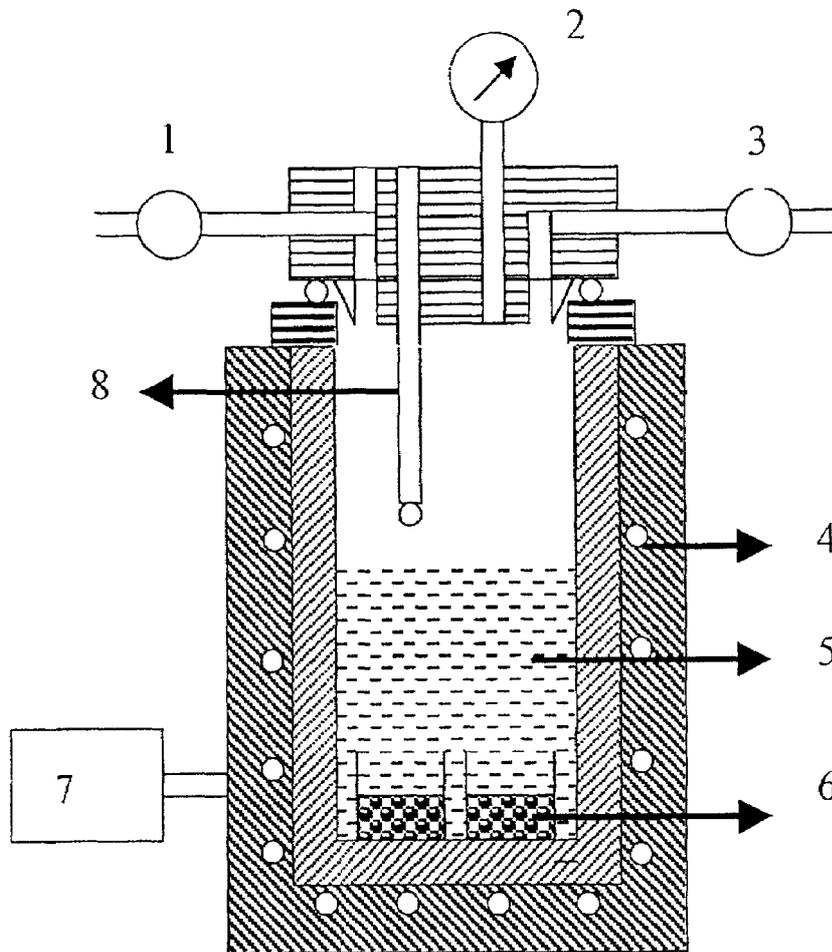


Fig.14: Autoclave for preparation of barium titanate and lead titanate by hydrothermal method

- (1) Gas in let (2) Pressure gauge (3) Vapour out let (4) Heater  
 (5) Alcohol (6) Alcogel (7) Temperature control (8) Thermocouple

### II.3. Equipment and Instrumentations

In the present study, the following equipments and instrumentations are used:

- **X-ray diffraction analysis**

X-ray diffraction patterns were investigated using a Brucker axes D8 advance using CuK  $\alpha$  radiation ( $1.5406\text{\AA}$ ) with a typical scanning begin at  $2\Theta$  equal to  $20^\circ$  to  $80^\circ$  and scan rate of  $20\text{ min}^{-1}$  was used for determination the phase formed . The crystallite size of barium titanate and lead titanate nanopowders was estimated from X-ray diffraction data using the Debye-Scherrer formula:

$$d_{RX} = k\lambda/\beta \cos \theta \quad (14)$$

Where  $d_{RX}$  is the crystallite size,  $k = 0.9$  is a correction factor to account for particle shapes,  $\beta$  is the full width at half maximum (FWHM) of the most intense diffraction peak,  $\lambda$  is the wavelength of Cu target =  $1.5406\text{\AA}$ , and  $\theta$  is the Bragg angle. The most intense peak (110) in case of BT and (101) in case of PT was used to calculate the crystallite size. The conversion (phase formation), % of barium titanate powders was estimated qualitatively from XRD results using the relationship:

$$\% \text{ Conversion} = \frac{I_1}{I_1 + I_2 + I_3} \times 100 \quad (15)$$

Where:  $I_1$ ,  $I_2$  and  $I_3$  are the intensities of the main peaks of various phases (Khedr et al, 2007).

- **Scanning Electron Microscope (SEM/EDX):**

The sample were characterized by scanning electron microscope using a JEOL instrument (Japan) model JSM-5410 scanning microscope was used for determine the microstructure of the obtained materials. A little amount of the as- prepared powders dispersed in alcohol were placed on aluminum stage especially made for scanning electron microscope. The samples were sputter-coated with Au. An accelerating voltage of 20 KV was used. The barium and titanium contents of the powders were determined by energy dispersive analysis of x-rays (EDAX) technique. The EDAX patterns were taken on the JSM- 5410 scanning electron microscope.

- **Fourier Transform Infrared Spectroscopy (FT-IR)**

The Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FT-IR-460 pluse Japan. The existence of organic compounds and lattice water incorporated of excess hydroxide species on the samples. IR spectra were recorded in the range of 400-4000  $\text{cm}^{-1}$ . The IR spectra were measured on samples in KBr pellets. The samples were ground with KBr (1:100 ratios).

- **Transmission Electron Microscope (TEM)**

The morphology and crystallographic information of the obtained powders were investigated by transmission electron microscope (JEOL, JEM-1230 operating at (80.00) KV. The powders were deposited on a copper- grid supported transparent carbon foil.

**Morphology:** The size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters.

**Crystallographic Information:** The arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter.

- **Dielectric Properties**

The dielectric properties were measured using HIOKI 3532-50 LCR HiTester; Japan. The test frequencies are set from 42 Hz to 5 MHz at high resolution. The electrical measurements were carried out through the powder which was pressed into pellets have 6 mm in thickness and 10 mm in diameter. Silver paste was used to ensure the good contact between the sample surfaces and the stainless steel electrodes of the cell capacitor. The measurements were carried out at the temperature range from 25 to 150°C.

## **II.4. Statistical design (Box-Behnken design)**

For preparation of barium titanate ( $\text{BaTiO}_3$ ) using organic carboxylic acid precursor and hydrothermal method, the experimental design, Box-Behnken design, was used to study the effect of studied variables for optimization procedure. For organic carboxylic acid precursor, the variables studied were calcination temperature, calcination time, and oxalic acid mole ratio which related to reacted with  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  ions. For hydrothermal method, the variables conditions were hydrothermal temperature, hydrothermal time, and pH of the solution. The response variables were barium titanate conversion  $\text{BaTiO}_3$  % and average crystallite size of barium titanate.

The design – matrix of different runs, 15 experiments, as well as the level of each factor are shown in Table 9

Table 9: Box- Behnken design with 3 levels and 3 variables

Run No.	Coded Factor Levels		
	Temperature	Time	Oxalic acid mole ratio
1	-1	-1	0
2	+1	-1	0
3	-1	+1	0
4	+1	+1	0
5	-1	0	-1
6	+1	0	-1
7	-1	0	+1
8	+1	0	+1
9	0	-1	-1
10	0	+1	-1
11	0	-1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0

As presented in Table 10 and Table 11, the factors of the highest confidence levels were prescribed into three levels, coded -1,0, and +1 for low, middle and high concentration (or values), respectively.

Table 10: The levels of variables chosen for the Box-Behnken optimization experiments by organic carboxylic acid precursor

<b>Variables</b>	<b>-1</b>	<b>0</b>	<b>+1</b>
<b>Temperature, °C</b>	800	1000	1200
<b>Time, hrs</b>	0.5	2.25	4
<b>Oxalic acid mole ratio</b>	0.5	1	1.5

Table 11: The levels of variables chosen for the Box-Behnken optimization experiments by hydrothermal method

<b>Variables</b>	<b>-1</b>	<b>0</b>	<b>+1</b>
<b>Temperature, °C</b>	150	175	200
<b>Time, h</b>	12	18	24
<b>pH</b>	12	13	14

According to this design, the optimal conditions were estimated using the factors and the response variable (conversion or phase formation of BaTiO<sub>3</sub> powders %) was generated.

The general form of the Equation is:-

$$E(y) = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} x_i x_j + \sum_{i=1}^3 \beta_{ii} x_i^2 \quad (16)$$

Where Y estimate of the response variable, X<sub>i</sub> are the independent variables of calcination temperature, calcination time and oxalic acid mole ratio for organic acid precursor and hydrothermal temperature, hydrothermal time, and pH of the solution for hydrothermal method that are known for each experimental run, and β<sub>0</sub>, β<sub>i</sub>, and β<sub>ij</sub> are the regression parameters or can be expression by the following Equation.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (17)$$

Where β<sub>0</sub> model constant; X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> independent variables; β<sub>1</sub>, β<sub>2</sub> and β<sub>3</sub> are linear coefficients; β<sub>12</sub>, β<sub>13</sub> and β<sub>23</sub> are cross product coefficients and β<sub>11</sub>, β<sub>22</sub> and β<sub>33</sub> are the quadratic coefficients (Smith, 1998; Abdel-Fattah et al, 2005; and Abdel –Aal et al, 2007).

Software package, Design-Expert 6.1, Stat-Ease, Inc., Minneapolis, USA, was used for regression analysis of experimental data and to plot response surface. Analysis of variance (ANOVA) was used to estimate the statistical parameters. The extent of fitting the experimental results to the polynomial model equation was expressed by the determination coefficient,  $R_2$ . F-test was used to estimate the significance of all terms in the polynomial equation within 95 % confidence interval.