

Chapter 2

Preparation of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ Solid Solution

2.1 Introduction

$\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) is ferroelectric at room temperature for the barium-rich compositions. It has the perovskite structure with a general formula ABO_3 in which A and B are cations at the different sites, A site and B site respectively. For BST, Ba and Sr are in the A site and Ti in B site.

In the past researchers prepared BST ceramics by conventional technique. The mixed oxides of BaCO_3 , SrCO_3 , and TiO_2 were weighed in a stoichiometric ratio and then milled. After calcining at 1100°C for 2 hours in air (17), the powder then was remilled with a small amount of polyvinyl alcohol (PVA) acted as a binder and pressed to form disk-shaped samples. The samples were sintered at 1250°C - 1430°C in air (18) after the binder was burned out. It was found that the density was up to 90% of the theoretical density. As the molar fraction of strontium increased, the average grain size and the lattice constant decreased (17-18). This is attributed to the smaller ionic radius of Sr^{2+} compared to that of Ba^{2+} , 1.16 and 1.36 Å respectively. Furthermore, the phase transition occurred at a lower temperature (17). For $x > 0.3$, the phase transition temperature of this composition decreased to lower than room temperature (17-18). As the grain size decreased, the remaining internal stress due to ferroelectric deformation became more difficult to release. The remaining internal stress varied in value to a larger extent, leading to a larger distribution width of phase transition temperature. Hence, the Curie peak broadened and dielectric constant at the ferroelectric state was higher (19-20). In Liou's work (17), the dielectric constant of BST increased as the molar fraction of strontium increased, but the maximum

dielectric constant of some compositions decreased as the strontium content is increased depending on their microstructures.

2.2 Preparation

The solid solutions of $Ba_{1-x}Sr_xTiO_3$ for this research were prepared by mixing and calcining all oxides and carbonates. These compositions studied in these system were

- a) $BaTiO_3$; $x=0$
- b) $Ba_{0.9}Sr_{0.1}TiO_3$ or BS1T; $x=0.1$
- c) $Ba_{0.8}Sr_{0.2}TiO_3$ or BS2T; $x=0.2$
- d) $Ba_{0.7}Sr_{0.3}TiO_3$ or BS3T; $x=0.3$

Conventional powder processing techniques were employed to prepare the bulk samples. Stoichiometric amounts of the chemically pure barium carbonate (99.9%), strontium carbonate (99.9%) and titanium dioxide (99.9%) were weighed and then wet ball-milled with ZrO_2 grinding media and ethyl alcohol as a solvent in a high density polyethylene bottle for 6 hours. Then the mixtures were dried and characterized by DTA (differential thermal analysis) to determine the suitable calcining temperature at which the complete carbonate decomposition occurred. After calcination with a heating rate of $2^\circ C/min$, the mixtures were retested by DTA to investigate the remaining reactions whether they were present. After there were no remaining reactions existing, the phase of calcined powder was also detected by powder X-ray diffraction.

The calcined materials were milled and 2% weight of PVA were added in the last hour of milling. The powder which had been sieved through 100-mesh was pressed into a disk of 13 mm. diameter by a single action dry-press with pressure of 80-85 MPa.

After burning-out binder with a heating rate of $1^{\circ}\text{C}/\text{min}$ and holding at 550°C in oxygen for 90 minutes, the disks were weighed before and after sintering to determine the weight loss. Then the disks were sintered with a heating rate of $4^{\circ}\text{C}/\text{min}$ and one hour soaking period at the maximum sintering temperature. Sintering temperature 1300°C , 1350°C and 1400°C were employed in this work. Then, the sintered samples were cooled in the furnace.

2.3 Differential Thermal Analysis (DTA)

2.3.1 Measurement

The powders before and after calcination of BaTiO_3 and $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ were characterized by PERKIN-ELMAR DTA7. The data were collected from 100°C to 1100°C with a heating rate of $10^{\circ}\text{C}/\text{min}$ in oxygen atmosphere.

2.3.2 Results and Discussions

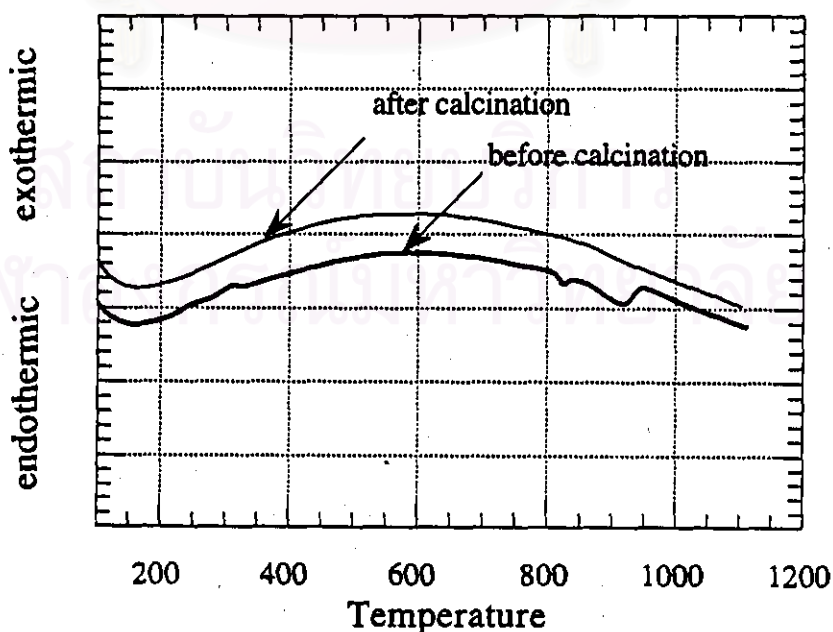


Fig 2.1 DTA curves of BaTiO_3 before and after calcination

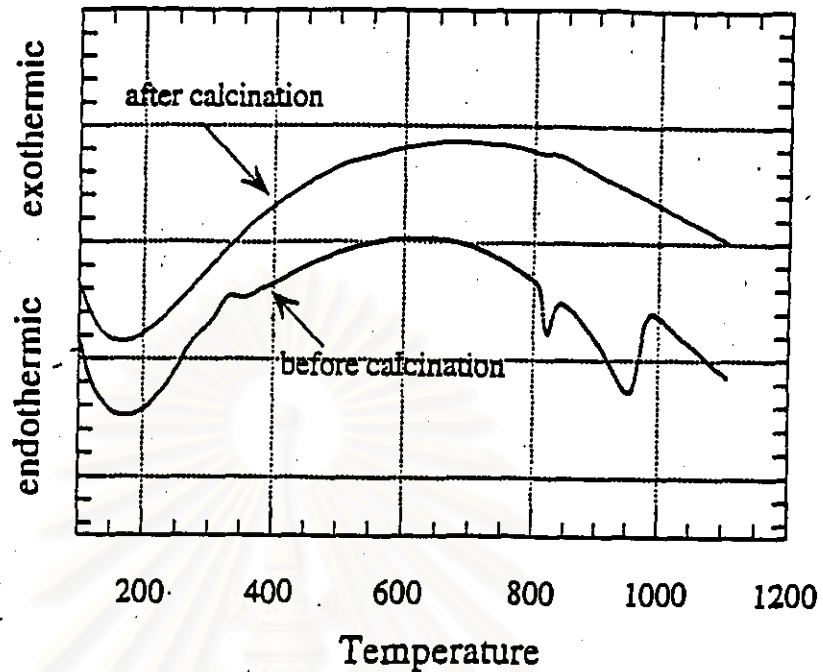


Fig 2.2 DTA curves of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ before and after calcination

From the DTA results in Fig 2.1 and Fig. 2.2, the reactions completed at 950°C for BaTiO_3 and 980°C for $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$. In this experiment the powders were calcined at 1050°C and also soaked at this temperature for 2 hours for a large amount of powder to complete the reactions. After calcining; the mixtures were retested by DTA. There were no peak observed in the calcined powder as shown in Fig 2.1 and 2.2. These results indicated that all reactions were finished after calcining at 1050°C .

2.4 X-ray analysis

The crystal structures at room temperature of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ are tetragonal for $x=0$ and 0.25, and cubic for $x=0.5$, 0.75 and 1.0 (17). For $x=0$ and 0.25, ferroelectric of BST changes to a paraelectric at $120^\circ\text{C} \pm 10^\circ\text{C}$ and $35^\circ\text{C} \pm 5^\circ\text{C}$, respectively.

The XRD patterns at room temperature of 1.0 mol% MgO and 0.05 mol% MnO₂ doped BST solid solution showed a single phase as shown in Fig 2.3 (17). MgO and MnO₂ acted as grain growth inhibitors. XRD results indicated that Ba_{1-x}Sr_xTiO₃ with x=0 and x=0.25 had the tetragonal structure. However, with x=0.5, 0.75 and 1.0 their structures became cubic since there was no splitting for all hkl. The lattice parameters of BST were calculated as listed in Table 1.

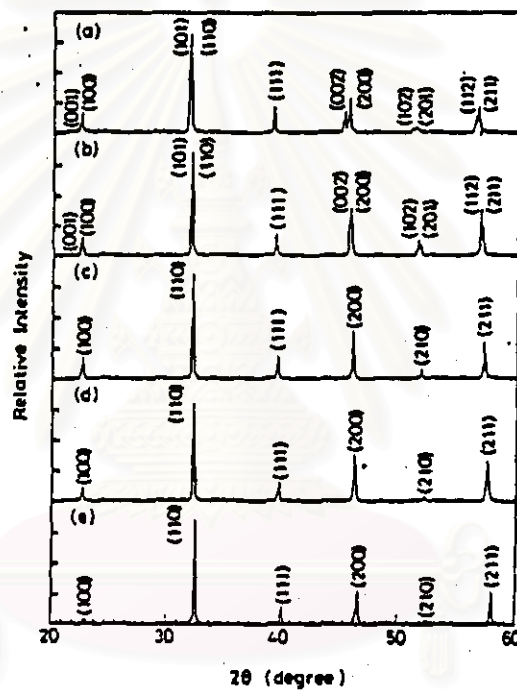


Fig 2.3 XRD patterns for Ba_{1-x}Sr_xTiO₃ doped with 1.0 mol% MgO and 0.05 mol% MnO₂ a) x=0 , b) x=0.25 , c) x=0.5 , d) x=0.75 and e) x=1.0 (17)

The average grain size of these compositions decreases with an increase in strontium. These values range from 14 to 2 μm which x= 0 up to x=1.0.

Basically, the X-ray diffraction is used to determine the lattice parameters and the crystal structure of the sample. The Bragg's angles determine the lattice

parameter and intensities identify the type of elements. The collection of this data is a critical operation because the preferred orientation effects in the X-ray patterns.

Table 1 Structure, Lattice Constant and Unit Cell Volume of 1.0 mol%MgO and 0.05mol%MnO₂-doped Ba_{1-x}Sr_xTiO₃ System (17)

| Strontium Molar Fraction (x) | Lattice Constant (Å) | Structure | Volume of Unit cell (Å) ³ |
|------------------------------|----------------------|------------|--------------------------------------|
| 0 | a=3.994 , c=4.032 | tetragonal | 64.32 |
| 0.25 | a=3.980 , c=3.992 | tetragonal | 63.23 |
| 0.5 | a=3.960 | cubic | 62.10 |
| 0.75 | a=3.931 | cubic | 60.74 |
| 1.0 | a=3.905 | cubic | 59.55 |

2.4.1 Measurement

The calcined powders of Ba_{1-x}Sr_xTiO₃ were sieved through a 100-mesh screen and mixed with standard silicon powder. Then the powders were pressed in sample holder and characterized by X-ray diffractometer Model JDX 3530, JEOL. The data were collected at room temperature with step angle of 0.02° and a counting time of 1 second. The setup conditions were

| | |
|----------------|-------|
| -Voltage (kV) | 40.00 |
| - Current (mA) | 40.00 |
| - Target name | Cu |

Results and Discussion

The XRD results in Fig.2.4 (a) show a single phase for all these compositions.

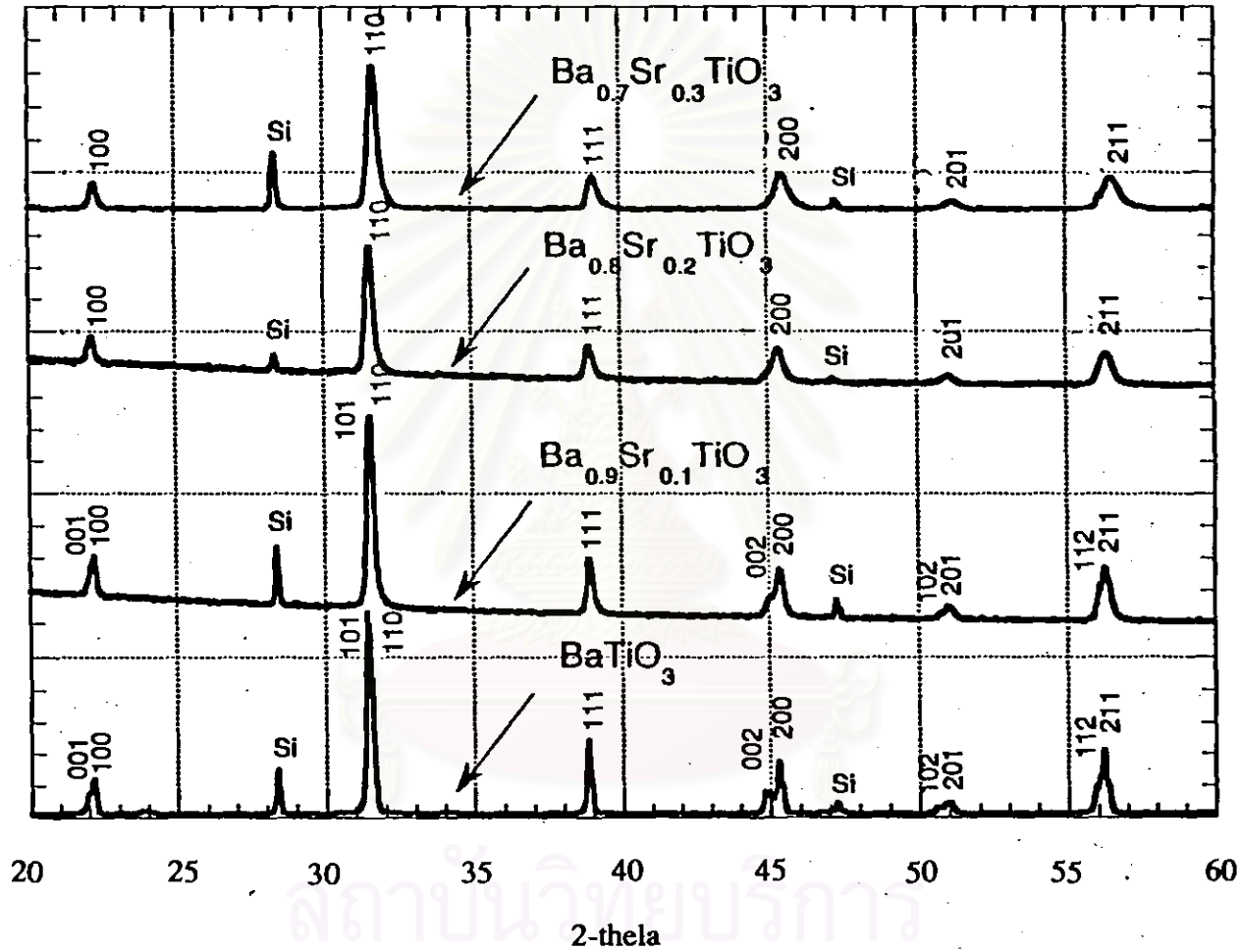


Fig. 2.4(a) XRD pattern of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ for $20^\circ \leq 2\theta \leq 60^\circ$

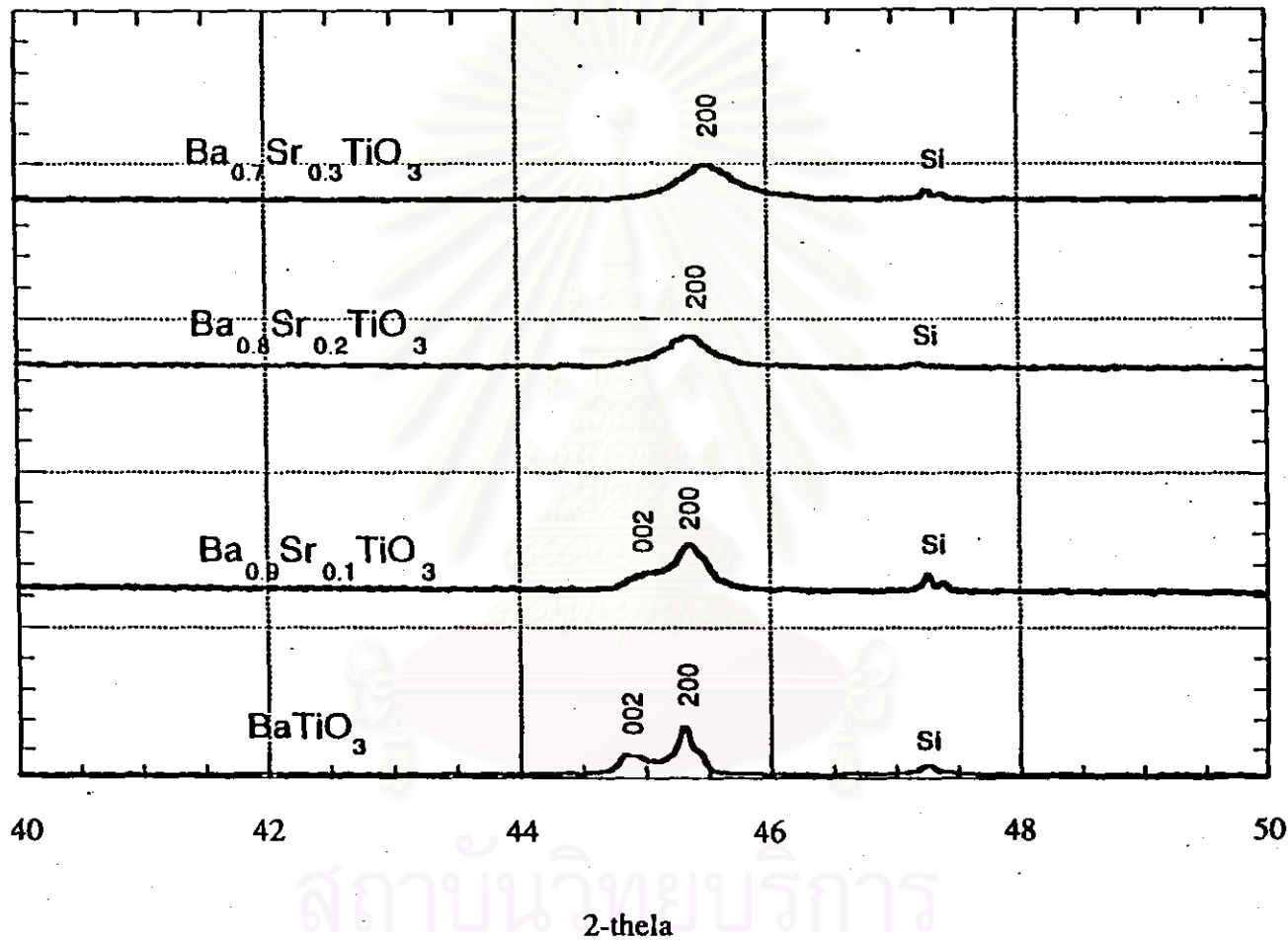


Fig. 2.4(b) XRD pattern of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ for $40^\circ \leq 2\theta \leq 50^\circ$

The splitting of (002) and (200) peaks shows tetragonal phase for BaTiO_3 . If both peaks shift closer, the tetragonal phase is reduced and changed to cubic phase. The XRD results are shown in Fig. 2.4(b), indicating that the (002) and (200) change from two peaks to one peak when the amount of strontium molar fraction of x is increased. The structures of BaTiO_3 and $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ are tetragonal due to the splitting of (200). In contrast to $x = 0.2$ and 0.3 , their structures become cubic since there is only one peak existing. These results are different from Liou and Chiou's work (17) that BST shows the tetragonal structure with $x \leq 0.25$. The lattice constants of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ are calculated as listed in Table 2.

Table 2 Lattice parameter and aspect ratio of calcined $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ system

| Strontium molar fraction | Lattice constant (\AA°) | c/a ratio | X-ray Density |
|--------------------------|---|-----------|---------------|
| $x=0$ | $a=4.004$ $c=4.048$ | 1.011 | 5.97 |
| $x=0.1$ | $a=3.996$ $c=4.030$ | 1.008 | 5.89 |
| $x=0.2$ | $a=3.990$ | - | 5.84 |
| $x=0.3$ | $a=3.984$ | - | 5.74 |

From Table 2, the lattice constant decreases with increasing strontium molar fraction. The lattice constants of undoped BaTiO_3 are 4.004 \AA° and 4.048 \AA° , which are different from these in Liou and Chiou work ($a=3.994 \text{ \AA}^\circ$ and $c=4.032 \text{ \AA}^\circ$). This may be due to MgO and MnO_2 affecting the lattice parameter of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ in his work. However, the c/a ratio of this experiment is closed to that of Liou and Chiou's work.

2.5 Weight Loss and Density After Sintering

2.5.1 Measurement

The weight loss was determined from the weight before and after sintering.

The bulk density was determined by Archimedes method. The sintered sample was dried and its dry weight, W_1 , was determined. Then the sample was kept in a suitable vacuum-pressure vessel at 90 kPa for 30 minutes. Allow the water to cover the sample and maintain the pressure at 90 kPa for one hour. After releasing the pressure, the suspended weight (W_2) and saturated weight (W_3) were determined. The bulk density was calculated from the following equation.

$$\text{bulk density} = \frac{W_1 \times \rho_0}{W_3 - W_2}$$

where ρ_0 is a density of water at room temperature

The theoretical density in this research is determined from the ratio of bulk density to the x-ray density.

2.5.2 Results and Discussion

The results of the weight loss and density as functions of firing temperature and soaking time for all compositions are shown in Table 3. As the sintering temperature and soaking time increase, the weight loss tends to increase. The weight loss of BaTiO_3 sintered at 1300°C and 1350°C is about the same, 0.9%. However, sintered at 1400°C the weight loss increases to 1.1%. This is probably due to the vacancies of oxygen taken place in BaTiO_3 . Higher sintering temperature influences the loss of oxygen from the material.

In addition, increasing soaking time affected an increase of weight loss. Longer soaking time tended to increase the weight loss as shown in Table 3.

Table 3 Weight loss and density versus temperature, soaking time and composition of $Ba_{1-x}Sr_xTiO_3$

| BaTiO ₃ | | | | |
|-------------------------|--------------|--------|----------------------|--------|
| Firing Temperature (°C) | %Weight loss | | %Theoretical density | |
| | 30 mins | 1 hour | 30 mins | 1 hour |
| 1300 | 0.9 | 1.1 | 97 | 96 |
| 1350 | 0.9 | 1.1 | 98 | 97 |
| 1400 | 1.1 | 1.7 | 98 | 97 |

| 0.9BaTiO ₃ -0.1SrTiO ₃ | | | | |
|--|--------------|--------|----------------------|--------|
| Firing Temperature (°C) | %Weight loss | | %Theoretical density | |
| | 30 mins | 1 hour | 30 mins | 1 hour |
| 1300 | 0.9 | 1.0 | 95 | 95 |
| 1350 | 1.0 | 1.2 | 96 | 95 |
| 1400 | 1.4 | 1.6 | 96 | 95 |

| 0.8BaTiO ₃ -0.2SrTiO ₃ | | | | |
|--|--------------|--------|----------------------|--------|
| Firing Temperature (°C) | %Weight loss | | %Theoretical density | |
| | 30 mins | 1 hour | 30 mins | 1 hour |
| 1300 | 1.1 | 1.3 | 97 | 95 |
| 1350 | 1.2 | 1.4 | 97 | 96 |
| 1400 | 1.5 | 1.9 | 96 | 95 |

| 0.7BaTiO ₃ -0.3SrTiO ₃ | | | | |
|--|--------------|--------|----------------------|--------|
| Firing Temperature (°C) | %Weight loss | | %Theoretical density | |
| | 30 mins | 1 hour | 30 mins | 1 hour |
| 1300 | 0.7 | 1.0 | 97 | 96 |
| 1350 | 0.8 | 1.0 | 97 | 96 |
| 1400 | 1.0 | 1.0 | 97 | 97 |

In general, the higher sintering temperature and longer soaking time increase the density until the maximum density is achieved. Above the optimum temperature it starts decreasing. The differential rates of densification and grain growth may produce an inhomogeneous microstructure of the samples (23).

The density values of this experiment are approximately 95-98% of the x-ray density as shown in Table 3. The results show that not only the sintering temperature and soaking time but the dopant also affect the densification of BaTiO_3 .



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