

# Phase and morphology investigation of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ( $x = 0.6, 0.7$ and $0.8$ ) powders

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## Abstract

This study aims to understand thoroughly the effects of calcining and sintering conditions on the relative permittivity and sintering behaviors of the solid solution method of preparing BSTs. BST ( $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ,  $x = 0.6, 0.7$  and  $0.8$ ) was synthesized using an established solid-state reaction method [R.K. Roeder, E.B. Slamovich, Stoichiometry control and phase selection in hydrothermally derived  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  powders, *J. Am. Ceram. Soc.* 82 (7) (1999) 1655, R. Ganesh, E. Goo, Microstructure and dielectric characteristics of  $\text{Pb}_x\text{Ba}_{0.5-x}\text{Sr}_{0.5}\text{TiO}_3$  ceramics, *J. Am. Ceram. Soc.* 79 (1996) 225, J.W. Liou, B.S. Chiou, Effect of direct-current biasing on the dielectric properties of barium strontium titanate, *J. Am. Ceram. Soc.* 80 (12) (1997) 3093, T. Noh, S. Kim, C. Lee, Chemical preparation of barium–strontium titanate, *Bull. Korean. Chem. Soc.* 16 (1995) 1180].  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  powders were used as starting materials. Crystallinity and lattice parameter of the calcined powders was improved by increasing the calcining temperature, as indicated by the increase in intensity of the X-ray diffraction peak. The particle size distribution also increasing at higher calcining temperature. The composition investigated here display dielectric properties characteristic of normal ferroelectrics.

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**Keywords:** Barium strontium titanate; Powders; Ceramics; Calcining; Sintering

## 1. Introduction

Ferroelectrics have become increasingly important as materials for electronic devices. The most widely used ferroelectrics occur in the perovskite family, with possess the general formula  $\text{ABO}_3$  and are characterized by compounds such as barium titanate ( $\text{BaTiO}_3$ ), strontium titanate ( $\text{SrTiO}_3$ ) and barium strontium titanate (BST) [1,2].  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  are known to form solid solutions across the entire compositional range due to their similar crystal structure and comparable ionic radii [3]. Solid solutions of BST are commonly used as capacitors in dynamic random access memory (DRAM) because of the high charge storage density, low leakage current, and resistance vs. time dependent dielectric breakdown [4]. The addition of strontium is usually employed to lower the Curie point

and maintain relatively low temperature dependence of the dielectric constant. However, knowledge of the effect of calcination and sintering conditions on the relative permittivity, sintering behavior and stoichiometric control is still quite limited.

The conventional method of synthesizing BST relies on solid-state reaction between  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{TiO}_2$  at high temperature. Unfortunately, this method has a tendency to produce coarse BST powders with compositional inhomogeneity and partial particle agglomeration. Thus, many workers use chemical processing method, such as sol–gel, co-precipitation, and oxalate addition for the preparation of pure single phase with small particle and homogeneous particle size distribution. However, almost all of these methods require high-purity inorganic or organic chemical as the starting materials, raising the cost above that conventional solid-state reaction that are more economical for large batch processing of these ferroelectric materials.

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This study aims to understand thoroughly the effects of calcining and sintering conditions on the relative permittivity and sintering behaviors of the solid solution method of preparing BSTs. Specifically, X-ray diffraction is used to characterize the phase transition of calcined BST powders. Analyses of the phase transition is used to support relative permittivity and sintering behavior data of  $Ba_xSr_{1-x}TiO_3$  ceramics.

### 2. Experiment

BST ( $Ba_xSr_{1-x}TiO_3$ ,  $x = 0.6, 0.7$  and  $0.8$ ) was synthesized using an established solid-state reaction method [4–7].  $BaTiO_3$  and  $SrTiO_3$  powders were used as starting materials. The powders were mixed by ball milling for 24 h with ethanol as a solution media. The mixed powders were dried at  $80^\circ C$  for 12 h then calcined at 1200, 1300 and  $1400^\circ C$  for 2 h. After calcining X-ray diffraction (Siemens, D500) and particle size analyzer (Malvern Masterizer), was employed to examine the phase constitution of the powders. Fine calcined powders were pressed into disc-shaped pellets at an isostatic pressure of 100 MPa. No binder was used. The firing of the green pellets was performed in a  $Al_2O_3$ -covered crucible at a temperature of  $1400^\circ C$  for 2 h. To determine the dielectric properties, the sintered

samples were polished to a thickness of 0.5 mm and provided with electrodes of silver paste applied to both surfaces and fired at  $900^\circ C$  for 1 h. The dielectric properties were measured using a HP4194A LCR meter at 1 kHz–1 MHz from  $25^\circ C$  to  $200^\circ C$ .

### 3. Results and discussion

XRD patterns and lattice parameter for the calcined powders at 1200, 1300, and  $1400^\circ C$  are shown in Figs. 1–3, respectively. These result indicated that highly crystalline phases were obtained at  $1200^\circ C$ . The XRD pattern showed all major X-ray reflection peak of perovskite BST phase, indicating the polycrystalline nature of powder with (1 1 0) as the major peak. Crystallinity of the calcined powders was improved by increasing the calcining temperature, as indicated by the increase in intensity of the X-ray diffraction peak. The lattice parameter of the powders also increased slightly with an increase in the calcining temperature. This indicates that at low calcining temperatures, the powders exist in more strained form with the atomic entities in non-equilibrium positions, which relax to the equilibrium positions at higher temperature. Another possible reason may be that the domain mobility is restricted due to pinning of the domain boundaries by crystal defects.

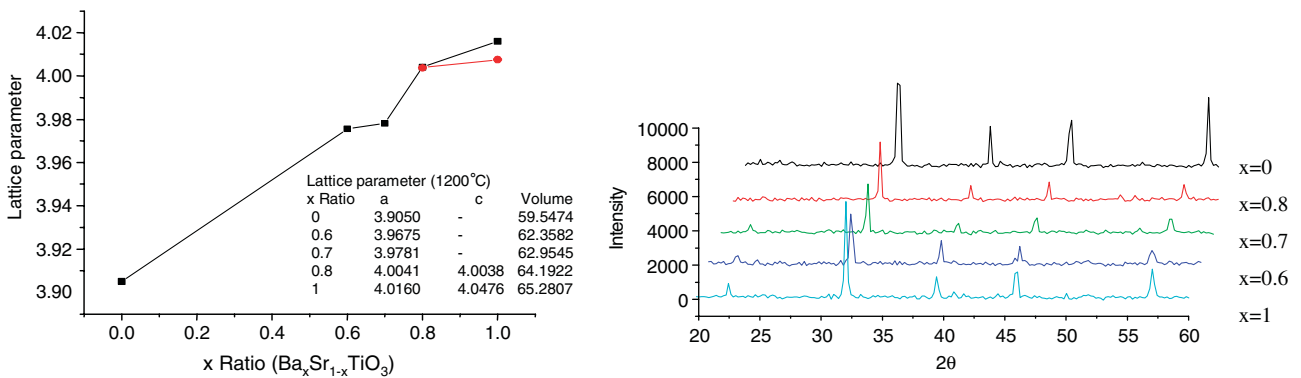


Fig. 1. Lattice parameters and XRD patterns of  $Ba_xSr_{1-x}TiO_3$  powders calcined at  $1200^\circ C$  for 2 h.

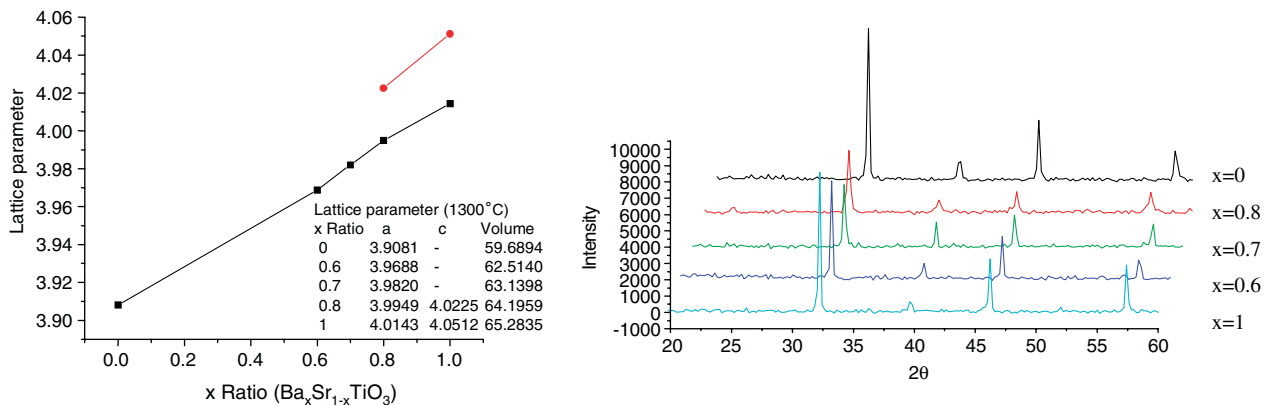


Fig. 2. Lattice parameters and XRD patterns of  $Ba_xSr_{1-x}TiO_3$  powders calcined at  $1300^\circ C$  for 2 h.

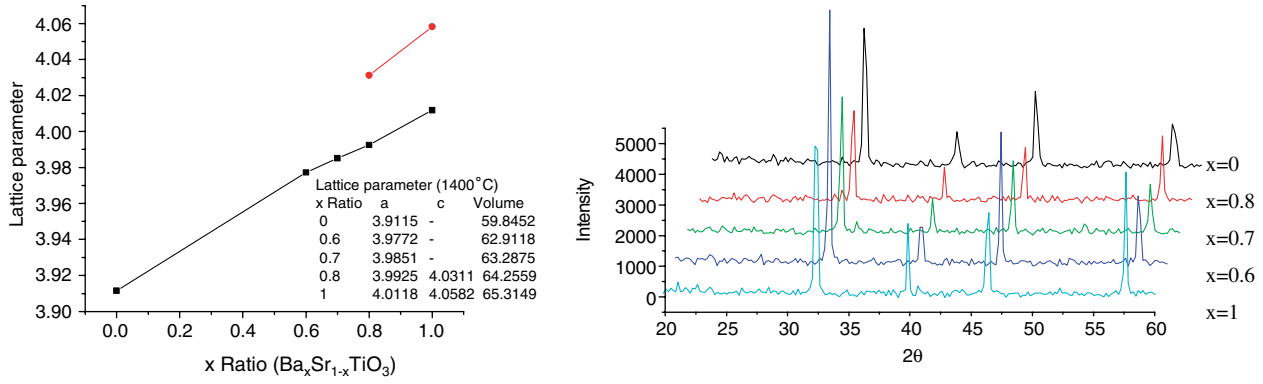


Fig. 3. Lattice parameters and XRD patterns of  $Ba_xSr_{1-x}TiO_3$  powders calcined at 1400 °C for 2 h.

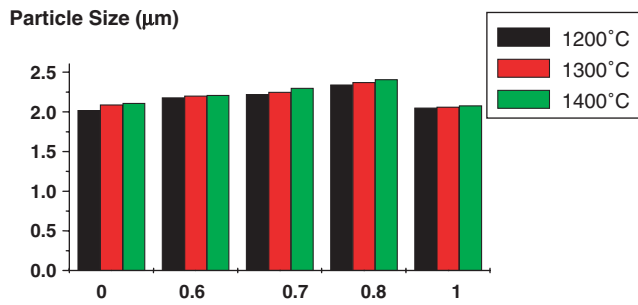


Fig. 4. Particle size of calcined  $Ba_xSr_{1-x}TiO_3$  powders at 1200, 1300, and 1400 °C for 2 h.

The particle size shown in Fig. 4 also increasing at higher calcining temperature.

The 1300 °C calcined powders were used to prepared BST ceramics. The bulk density of  $Ba_xSr_{1-x}TiO_3$ ,  $x = 0.6, 0.7,$  and  $0.8$  ceramics expressed as percent of theoretical was found to be 93%, 94%, and 94%, respectively. Figs. 5–7 show the temperature dependence of the dielectric properties of the BST samples without bias field. The dielectric permittivity frequency dispersion is weak. To observe the  $Ba_{0.6}Sr_{0.4}TiO_4$  phase transition, we plotted inverse  $\epsilon'$  with temperature (Curie–Weiss’s law) [1]. The phase transitions of  $Ba_xSr_{1-x}TiO_3$ ,  $x = 0.6, 0.7$  and  $0.8$

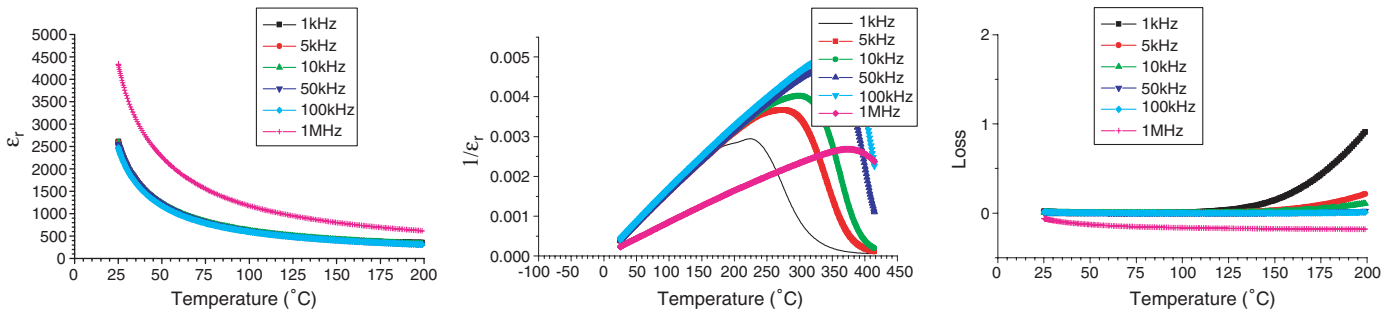


Fig. 5. Values of  $\epsilon'$ ,  $1/\epsilon'$ , and dielectric loss at various frequencies plotted as a function of temperature for  $Ba_{0.6}Sr_{0.4}TiO_3$  sintered at 1400 °C for 2 h.

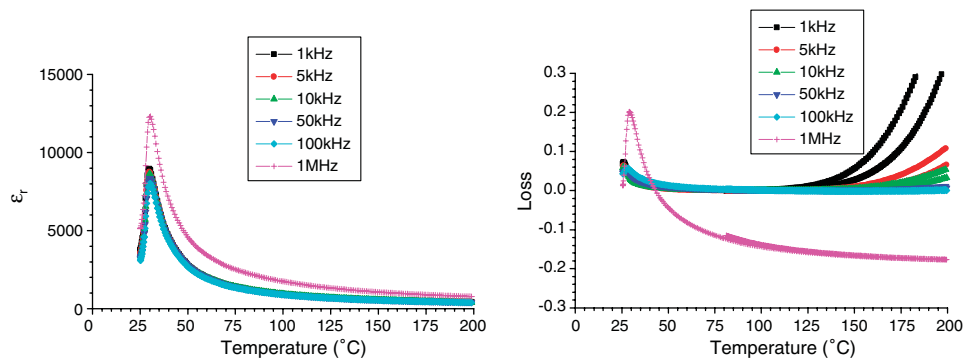


Fig. 6. Values of  $\epsilon'$ ,  $1/\epsilon'$ , and dielectric loss at various frequencies plotted as a function of temperature for  $Ba_{0.7}Sr_{0.3}TiO_3$  sintered at 1400 °C for 2 h.

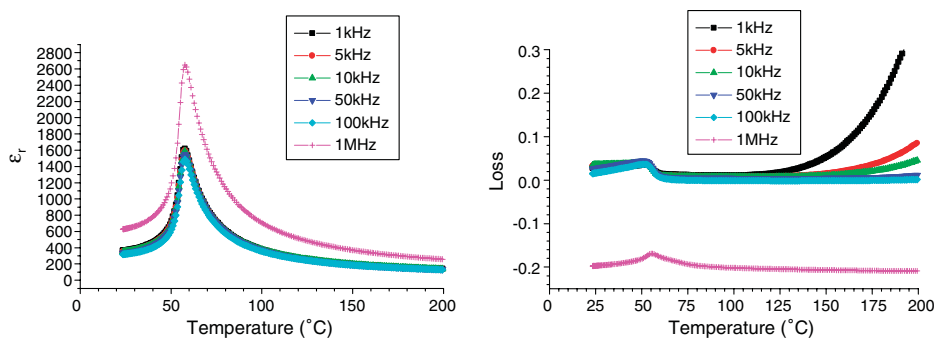


Fig. 7. Values of  $\epsilon'$ ,  $1/\epsilon'$ , and dielectric loss at various frequencies plotted as a function of temperature for  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  sintered at  $1400^\circ\text{C}$  for 2 h.

ceramics were found to be  $0^\circ\text{C}$ ,  $32^\circ\text{C}$  and  $61^\circ\text{C}$ , respectively. The transitions are broader and occur at lower  $\epsilon'$  peak when the  $x$  ratios are increasing. The composition investigated here display dielectric properties characteristic of normal ferroelectrics [1,2]. The sharp maxima and lack of frequency dispersion in the dielectric behavior observed for the  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  and  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  samples at the transition temperature can be ascribed to the uniform distribution of fine grains [8–10]. The dielectric data above 1 MHz are unreliable due to high frequency errors [9]. The dielectric loss also showed a peak at the transition temperature, which indicates a well-defined phase transition. Below 1 MHz, the values of  $\epsilon'$  decreased slightly with increasing frequency.

#### 4. Conclusions

The result of lattice parameter measurements and XRD patterns indicate that the perovskite phase of the  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ,  $x = 0.6, 0.7$ , and  $0.8$  system can be obtained by calcining at  $1200, 1300$ , and  $1400^\circ\text{C}$ . The particle size was observed to increase slightly at higher calcining temperatures and  $x$  ratios. The lattice parameter of the powders were also observed to increase slightly with increasing calcining temperature. In addition the Curie temperature were observed to increase with increasing  $x$  ratios. Below

1 MHz, the frequency dependence of  $\epsilon'$  was observed to decrease slightly with increasing frequency.

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