Synthesis of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics via hybrid method

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Abstract. Barium strontium titanate (BST) ceramics were prepared by the hybrid method between Solid-state reaction and Sol-gel combustion methods using urea as a fuel. The crystalline powders were prepared by the mixed precursors between Solid-state reaction: Sol-gel combustion with the molar ratio of 1:0.3 and calcined at 950^{o}C for 2 hours. The BST ceramics were fabricated from calcined powders by sintering at 1050-1350^{o}C and instigated the crystal structures by XRD. All sintering samples have a pure perovskite structure corresponding to JCPDS no. 34-0411. The SEM revealed an increasing of a gain size when with increasing sintering temperature. The highest dielectric constant 11580 was found in the sample prepared at 1350^{o}C for 4 hours with dielectric loss of 0.007.

1. Introduction

In recent years, research on barium strontium titanate (BST) has become very popular because of its prominent electrical properties, for example, high dielectric constant, low dielectric loss, and high tunability. It has been utilized in many applications such as sensors, actuators, and capacitors. In addition, several publications have appeared documenting that the microstructure and crystal structures of BST powders significantly depend on calcination temperatures and synthesis routes.

There is great effort which has been devoted to the study of crystalline BST powder synthesis methods such as hydrothermal [1], co-precipitation [2], solid-state reaction [3, 4] and sol-gel. In fact, sol-gel method [5] is one of the most interesting methods since the results offered by Thongchanthep and Thountom found that it gave high purity, small size and good uniformity crystalline powders at relatively low calcination temperatures [6]. Besides, solid-state reaction method is widely used due to its easy preparation. However, the crystalline powders prepared by the method is relatively large in particle size and to obtain the pure perovskite phase it requires somewhat high calcination temperatures, compared to other methods. From previous research, the BST powder prepared by solid-state reaction yields pure phase at the calcination temperature of 1180^{o}C and the BST powder prepared by sol-gel combustion method yields pure phase at the lower calcination temperature of 750^{o}C.

Therefore, this research opens up a new preparation method for synthesis BST ceramics by the hybrid method between sol-gel combustion method using urea as fuel and solid-state reaction method. The precursors from both were mixed in different ratios. The effects of sol-gel to solid-state reaction precursor ratios and calcination temperatures on the crystal structures and microstructure were studied.

2. Materials and method

2.1. Preparation of a BST precursor by solid-state reaction method and sol-gel combustion method

The chemicals, $BaCO_3$ (98.5%), $SrCO_3$ (99.5%), and TiO_2 (99%), were used as staring materials which were stoichiometrically mixed by ball-milling for 24 hours. After finishing this stage, the mixture was dried at 100°C for overnight. The dried powders were called SR.

Sol-gel combustion method, Citric acid was dissolved in deionized water and stirred; meanwhile, ammonium hydroxide was added to the previous solution until its pH was 9. $Ba(NO_3)_2$ (99%), $Sr(NO_3)_2$ (99%), and $C_{16}H_{36}O_4Ti$ (97%) were put in the solution and then the mixture was heated at 90°C for 4 hours. Subsequently, the equal molar proportion of urea to the mixture was added. As a result, the BST sol-gel combustion precursor (SC) was obtained.

The solid-state reaction (SR) and sol-gel combustion (SC) precursors were mixed together at 1:0.3 in molar ratio. In order to obtain the crystalline BST powders, the mixture was calcined at the various temperatures (650, 750, 850, and 950°C) for 2 hours. Afterward, the BST powders were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques.

2.2. Preparation of BST ceramics

The pellets were made of BST powders at 1:0.3 (SR:SC) and sintered at 1050-1350°C for 4 hours. XRD, SEM, and dielectric tester were used to study the crystal structures, microstructures and dielectric properties, respectively.

3. Results and discussion

The crystal structure of the calcined powders at different ratios of SR:SC and calcination temperatures were illustrated in figure 1(a). The formation of perovskite structure and pyrochlores, ($BaCO_3$, $SrCO_3$, and TiO_2) is apparent at 650°C and over. Nonetheless, the pure phase of BST is found at the condition of 1:0.1, 1:0.2, and 1:0.3 (SR: SC) at 950°C for 2 hours. Figure 1(b) shows XRD spectrum of the BST ceramics sintered at 1050-1350°C for 4 hours. There is no pyrochlore phase detectable indicating that pure perovskite structure ceramics are successfully synthesized at every sintering temperature.

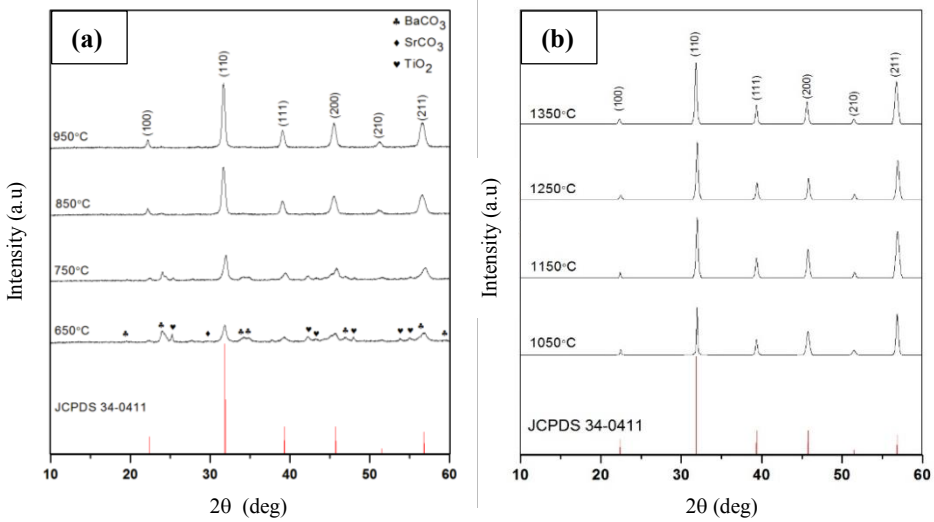

Figure 1. The XRD spectrum of BST ceramic (a) calcined at 650-950°C for 2 hours at SR: SC molar ratios of 1:0.3 and (b) sintered at 1050-1350°C for 4 hours.

Figure 2(a) shows SEM micrographs of BST powders (SR: SC= 1:0.3) calcined at 950°C for 2 hours. Spherical particles with agglomeration are found. The average particle size was about 112 nm.

Figures 2(b)-2(e) depict the grain micrographs of ceramics sintered at different temperature. As seen, the grain size developed when temperature increased since particles are integrated.

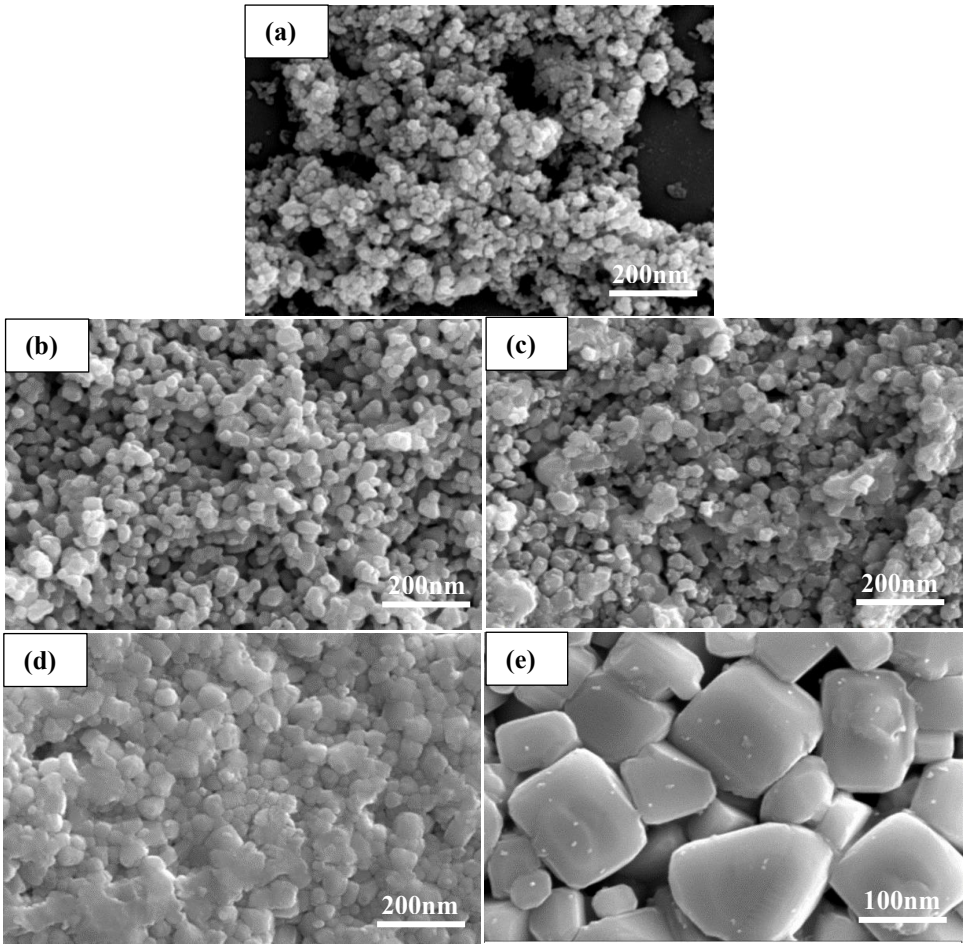

Figure 2. The SEM micrograph of (a) BST powders (SR: SC= 1:0.3) calcined at 950^{o}C for 2 hours and BST ceramic surfaces sintered at (b)1050^{o}C, (c)1150^{o}C, (d)1250^{o}C, and (e)1350^{o}C 4 hours.

Table 1. The average grain size, shrinkage, and density of BST ceramics at different sintering temperatures.

Sintering temperature(^{o}C)	Average grain size (μm)	Shrinkage (%)	Dielectric constant (at 1 kHz)	Dielectric loss (at 1 kHz)
1050	0.23	8.19	1136	0.305
1150	0.36	13.61	3465	0.108
1250	0.45	25.99	6008	0.085
1350	2.13	16.61	11580	0.007

The average grain size of synthesis ceramics was found increased corresponding with the increasing of sintering temperature [6] and reached 2.13 μm for the ceramic sintered at 1350^{o}C. In the same way, the shrinkage and the density also increased according to temperature raising. The effect of those factors on dielectric properties was significant, which the dielectric constant and dielectric loss of BST depended on the physical properties and the fabrication process of the ceramics, grain size, porosity, firing temperature [7]. Dielectric constant of BST ceramics increased with higher sintering

temperature used in contrast to dielectric loss. As can be seen from figure 3, the ceramic that sintered at 1350°C has the highest dielectric constant (11580) at room temperature while dielectric loss is approximately 0.007. From the result, the synthesis of BST ceramics via hybrid method have shown the higher dielectric constant than previous research [6].

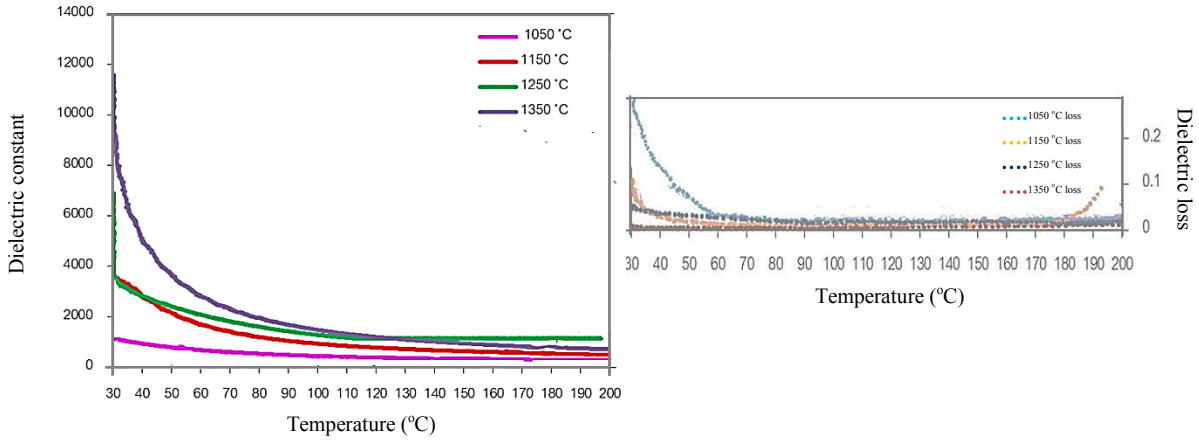

Figure 3. Dielectric constant and dielectric loss dependent on temperatures at frequencies 1 kHz of BST ceramics sintered at different temperatures for 4 hours.

Illustrated in table 2, annealing condition, average grain size and dielectric properties of BST ceramics prepared by different methods show that the sol-gel combustion and solid-state reaction hybrid method is comparatively effective to fabricate BST ceramics. Further, the samples prepared by sol-gel combustion and solid-state reaction hybrid method have higher dielectric constant than those prepared by sol-gel combustion, but have less dielectric constant than those prepared by solid-state reaction.

Table 2. The BST ceramics prepared by various methods

Method	Calcination temperature (°C)	Sintering temperature (°C)	Average grain size (μm)	Dielectric constant	Dielectric loss
Sol-gel combustion [6]	750	1350	3.93	4870	0.43
Solid-state reaction [8]	1180	1350	5.6	17900	0.04
Sol-gel combustion and Solid-state reaction Hybrid method	950	1400	2.13	11580	0.007

4. Conclusion

The BST ceramics were successfully fabricated by the hybrid method using urea as a fuel. In powders, the perovskite structure and pyrochlores ($BaCO_3$, $SrCO_3$, and TiO_2) were found at lower firing temperatures (550-850). However, the temperature for synthesizing the pure phase of BST powders was 950°C and above at 1:0.3 molar ratio of SR: SC. Particle sizes of the powder were in submicron range. Furthermore, pure BST ceramics were achieved from every sintering temperature. Grain size and density show an increase trend with the raising of temperature. Optimal dielectric properties were obtained from the ceramic sintered at 1350°C.

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