

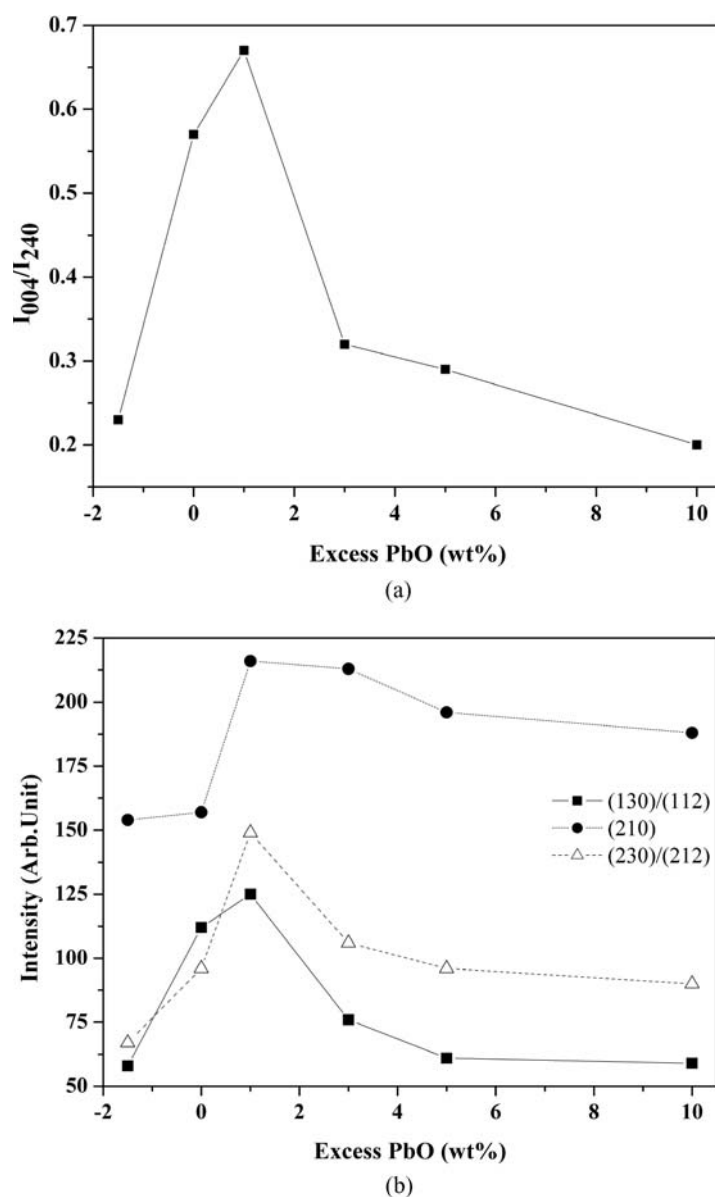


Figure 2. (a) value of intensity ratio, I_{004}/I_{240} for sintered pellets as a function of excess PbO; (b) relative intensity of (130)/(112), (210) and (230)/(212) XRD peaks as a function of excess PbO.

temperature are shown in Fig. 4. The 1 wt% excess PbO sample exhibits the maximum d_{33} and k_p of 52 pC/N and 0.34, respectively. It can be noted that the electrical properties of the ceramics can be related to the density of the samples. The values of sintered density as a function of PbO content are listed in Table 1. The maximum density was found for the 3 wt% samples which was $\sim 0.5\%$ higher than for the base composition. However, the density for the 1 wt% samples was found to be close to the 3 wt% samples. It can be assumed that the 1 and 3 wt% excess PbO produce the optimum density ceramics. For PbO deficient

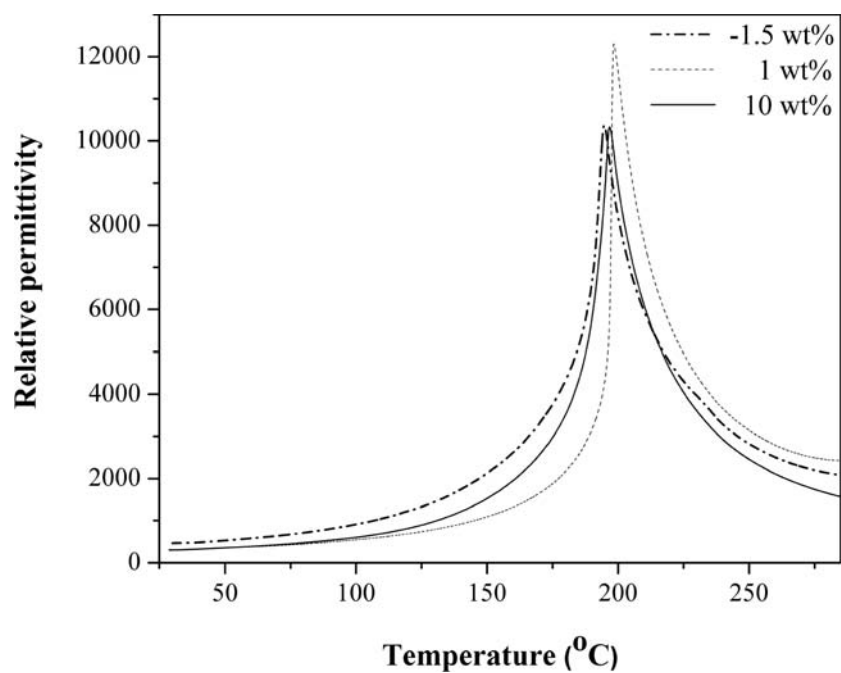


Figure 3. Relative permittivity versus temperature for PBZ10 made from powders with different amount of starting excess PbO.

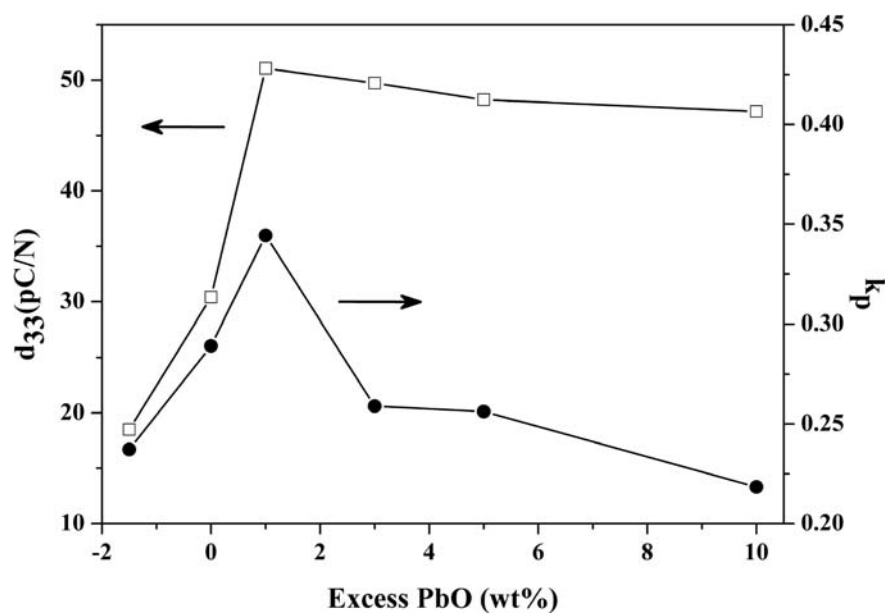


Figure 4. Piezoelectric properties of d_{33} and k_p in PBZ10 ceramics made from powders with different amount of starting excess PbO.

samples, the lower values of the electrical properties can be related to the presence of ZrO_2 as observed in the XRD patterns. However, the reduction of electrical properties in the 5, and 10 wt% samples match that of the trend of the sintered density. The lowering of density is consistent with there being an excessive amount of PbO in these samples which presents the PbO liquid phase during the sintering. A large amount of PbO liquid phase can produce an initial rapid densification but a lower final density as a result of void formation due to the PbO evaporation as a consequence the porosity of the pellet increases and this porosity is not removed by solid state sintering [14–16].

Conclusions

In the present work, PBZ10 ceramics were prepared by a conventional mixed oxide method with various excess PbO contents. Effect of deficient and excess PbO on phase formation and electrical properties of PBZ10 ceramic have been studied. The XRD results revealed that the fraction of the rhombohedral phase relative to the orthorhombic phase has effected by PbO content. The 1 and 3 wt% excess PbO were found to produce the maximum density which exhibited the maximum electrical properties of the ceramics.

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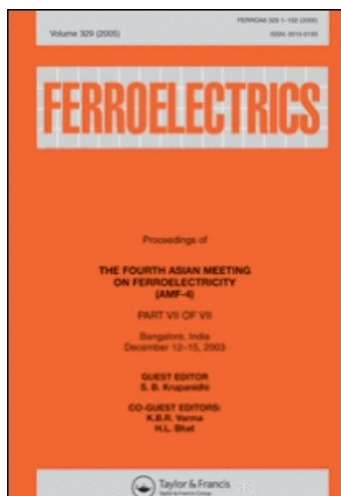
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Effect of Firing Temperatures on Phase Formation and Microstructure of $\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ Ceramics Prepared via Mixed Oxide Method

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Effect of Firing Temperatures on Phase Formation and Microstructure of $\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ Ceramics Prepared via Mixed Oxide Method

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$\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ (BZT) ceramics were fabricated by a mixed oxide synthetic route. The effect of calcination and sintering temperatures on phase formation and the microstructure of the ceramics were investigated. The pure perovskite phase of BZT powders was obtained with a calcination condition of 1300°C for 4 h. The sintered pellets showed a pure perovskite cubic phase in all samples. The microstructure of the powders exhibited an almost-spherical morphology and had a porous agglomerated form. The average particle sizes and the average grain sizes were increased from 0.2 to 1.1 μm and 3.9 to 25.1 μm with increasing calcination and sintering temperatures, respectively. The densest and the highest maximum dielectric constant was found in the BZT ceramic sintered at 1550°C.

Keywords Barium zirconate titanate; microstructure; phase formation; mixed oxide

Introduction

Barium titanate (BaTiO_3 , BT) is well known as a fundamental ferroelectric perovskite oxide [1] and is often used in multilayer ceramic capacitors (MLCs) due to its' high dielectric constant [2]. BaTiO_3 displays dielectric anomalies at 130, 0, and -90°C with respective transformations in symmetry from cubic to tetragonal, from tetragonal to orthorhombic, and from orthorhombic to rhombohedral, respectively. Those anomalies are accompanied by a high dielectric constant near the phase transition [3]. The nature and phase transition temperature of BT can be modified via the partial substitution of either Ba ions (A-site doping) or Ti ions (B-site doping). A-site doping with cations of the same valence as Ba causes the Curie temperature (T_c) ($\sim 130^\circ\text{C}$) to either decrease (Sr substitution) or increase (Pb substitution) without any significant broadening of the transition [4]. With B-site doping, the ferroelectric domains, which are associated with a cooperative

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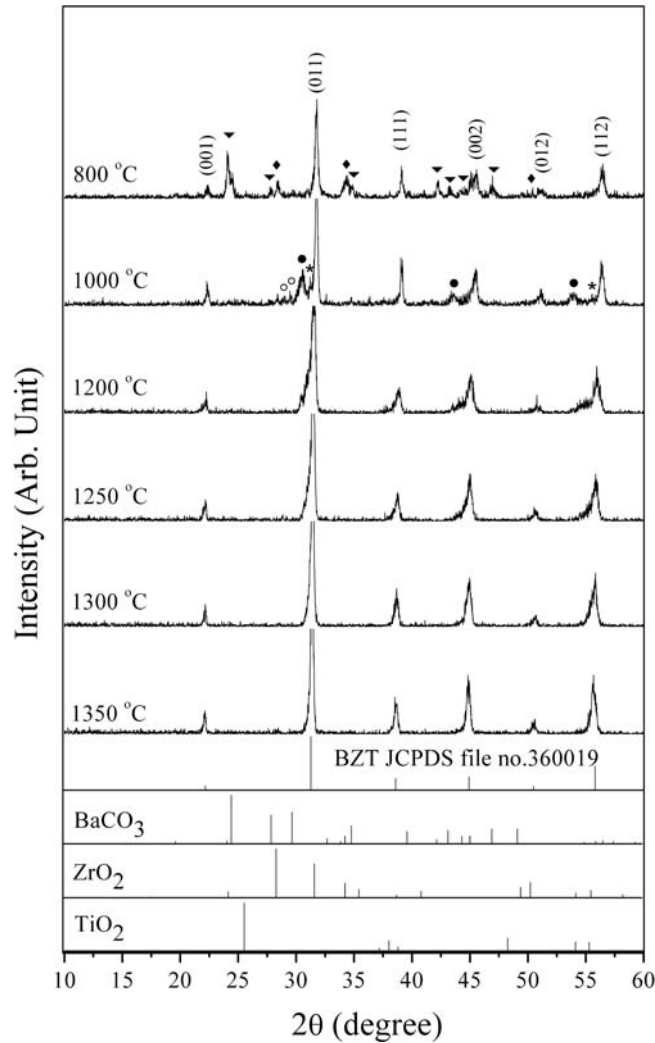


Figure 1. XRD patterns of $\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ powders: (▼) BaCO_3 ; (◆) ZrO_2 ; (●) BaZrO_3 ; (○) Ba_2ZrO_4 ; (*) BaTiO_3 .

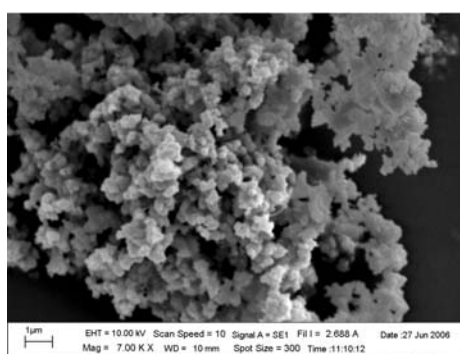
off-center displacement of Ti^{4+} ions in their TiO_6 octahedra, are disrupted, which often leads to a broadening of the transition at T_c . Partial replacement of titanium by tin or hafnium generally leads to a reduction in T_c and an increase in the permittivity maximum with dopant content [5].

Barium zirconate titanate ($\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$) is obtained by substituting ions at the B site of BaTiO_3 with Zr ions. This substitution results in a decrease in the temperature and a broadening of the permittivity maximum [6]. Brajer and Kulscar showed that, as the zirconium content increases, the orthorhombic-tetragonal phase transition temperature increases and the tetragonal-cubic phase transition temperature decreases [7, 8]. At a Zr/Ti ratio greater than 0.10, the three dielectric constant peaks coalesce into a single broad maximum [9]. $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ with $0.20 \leq x \leq 0.35$ ceramics were prepared by a sol-gel process [10]. The dielectric study of the ceramics showed a normal ferroelectric with weak

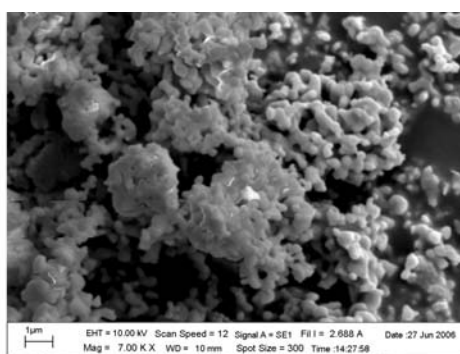
Table 1

The percent perovskite phase, average particle size, average grain size, T_c and density of BZT.

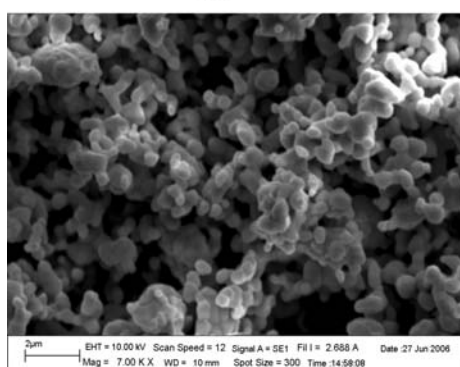
Calcined powders			Sintered ceramics			
Calcination temperatures (°C)	% perovskite phase (%)	Average particle size (μm)	Sintering temperatures (°C)	Average grain size (μm)	T_c (°C)	Density (g/cm^3)
800	68	0.26	1400	3.1	-64	5.70
1000	80	0.31	1450	7.2	-64	5.74
1200	83	0.79	1500	11.5	-63	5.78
1250	91	0.87	1550	12.2	-63	5.80
1300	100	0.91	1600	20.8	-92	5.69
1350	100	1.37				



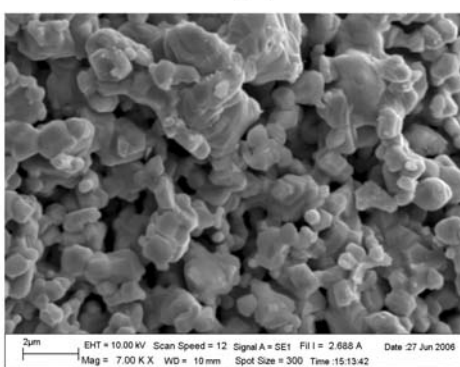
(a)



(b)



(c)



(d)

Figure 2. SEM photographs of BZT powders calcined at (a) 800°C, (b) 1200°C, (c) 1250°C and (d) 1350°C.

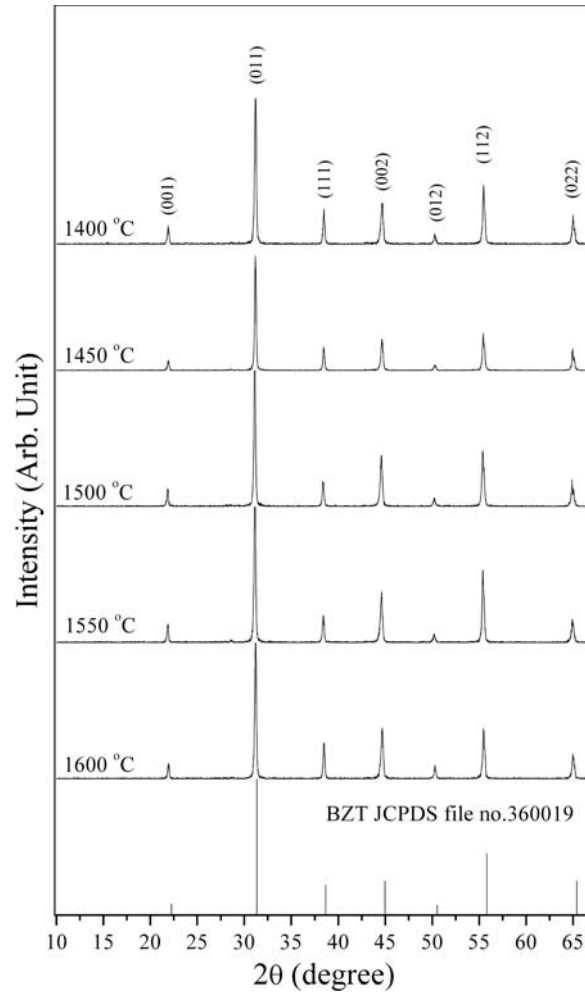


Figure 3. XRD patterns of Ba(Zr_{0.3}Ti_{0.7})O₃ ceramics.

diffuse phase transition behaviors for the ceramics with $x = 0.20$ and 0.25 [10]. The diffuse phase transition and a relaxor-like behavior were found at high Zr contents ($x = 0.30$ and 0.35). The tunability and dielectric loss of Ba(Zr_{0.3}Ti_{0.7})O₃ (BZT) ceramic measured at room temperature under the biasing field 40 kV/cm are 45% and 0.002, respectively [11]. This make the Ba(Zr_{0.3}Ti_{0.7})O₃; BZT ceramic promising material for tunable materials applications. However, to the author's best knowledge, the effect of firing temperature on crystal structure and morphology of Ba(Zr_{0.3}Ti_{0.7})O₃ powders and ceramics prepared by mixed oxide method have not been reported yet. Therefore, in the present work, the effect of calcination and sintering temperatures on microstructure and the phase formation of Ba(Zr_{0.3}Ti_{0.7})O₃ (BZT) ceramics prepared via a solid state reaction method was chosen. This would extend an understanding on the processing-properties relationships in the BZT ceramics.

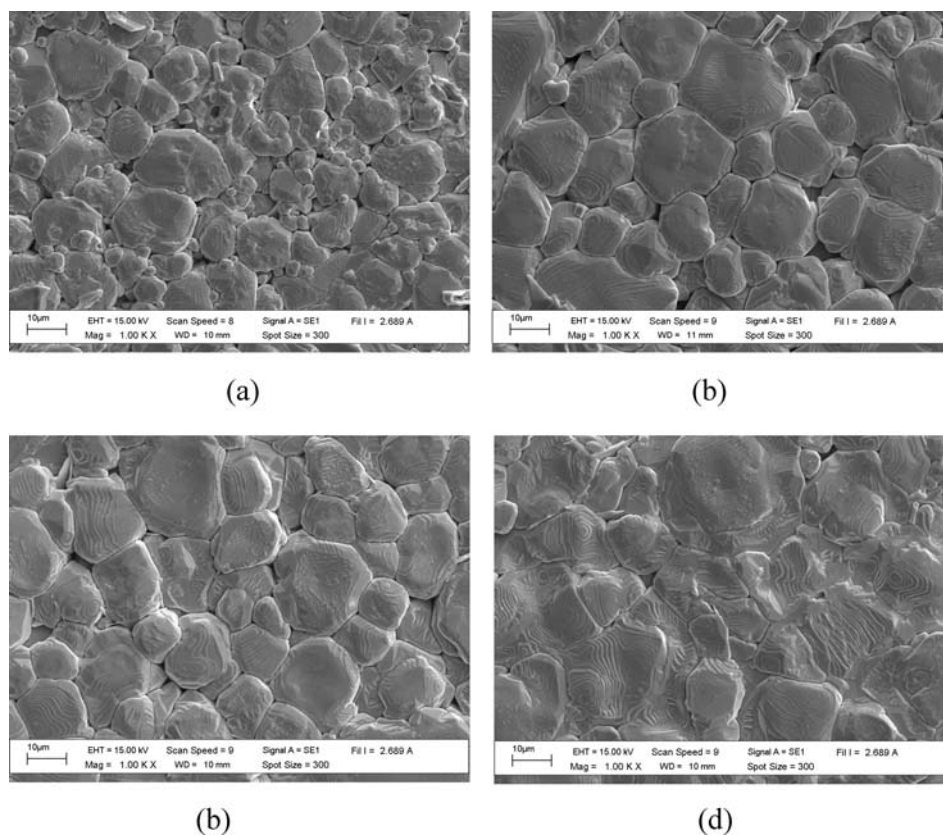


Figure 4. SEM photomicrograph of BZT ceramics sintered at (a) 1450°C, (b) 1500°C, (c) 1550°C and, (d) 1600°C.

Experimental

The starting materials were commercially available barium carbonate, BaCO_3 (99%) titanium (IV) oxide, TiO_2 (99%) and zirconium (IV) oxide, ZrO_2 (99%). Barium zirconate titanate ($\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$, BZT) powder was synthesized by the solid state reaction of thoroughly ground mixtures of BaCO_3 , TiO_2 and ZrO_2 powders by a ball milling procedure (zirconia milling media under ethanol for 24 h). Drying was carried out at 120°C for 4 h. After sieving, the mixture was calcined at various calcination temperatures, ranging from 800 to 1350°C, with a dwell time of 4 h and a heating/cooling rate of 5°C/min. The calcined powders were then pressed into disks with a diameter of 15 mm at a pressure of 40 MPa. The pellets were sintered from 1400 to 1600°C for 2 h and cooled in a furnace. For electrical measurements, silver paste was fired on both sides of the polished samples at 500°C for 30 min and used as electrodes.

X-ray diffraction (XRD; Philip PW3040/60 X' Pert Pro) was employed to identify the phase formed and optimum temperature of BZT powders and ceramics. Calcined powders and sintered ceramics morphologies were imaged using scanning electron microscopy (SEM; LEO 1455 VP). Densities of sintered ceramics were measured by Archimedes method and the average grain size was determined by using a mean linear intercept method. The capacitance was measured with a LCR meter (Agilent 4263B) ranging from –170 to

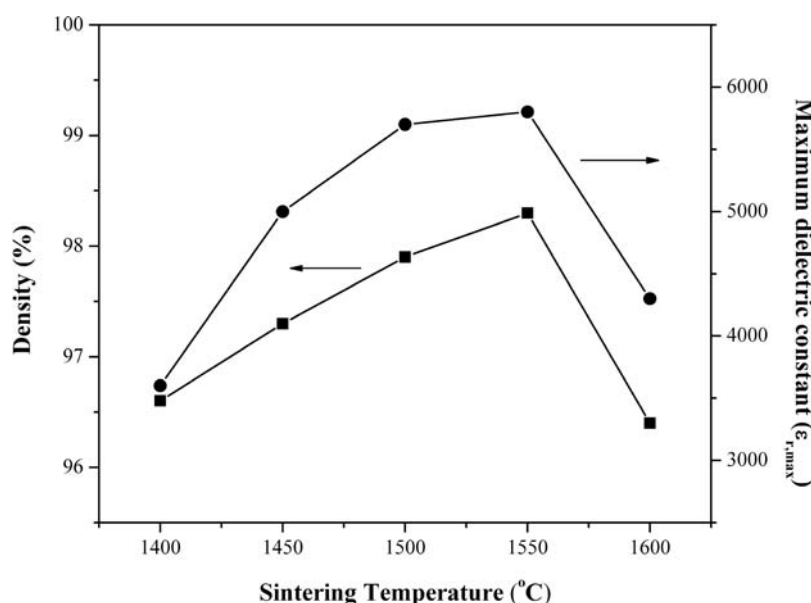


Figure 5. Variation of maximum dielectric constant and density of BZT ceramics as function of sintering temperatures.

25°C. The dielectric constant (ϵ_r) was calculated using the geometric area and thickness of the discs.

Results and Discussion

XRD patterns of BZT powders calcined at various temperatures are plotted in Fig. 1. After calcination at 800°C, the crystalline phase of BZT was accompanied with BaCO_3 and ZrO_2 as separate phases, whose X-ray peak matches the JCPDS file number 41-0373 [12] and 24-1165 [13]. As the temperature increased to 1000°C, the peaks corresponding to the raw materials disappeared, while the intensities of the BaTiO_3 , BaZrO_3 and Ba_2ZrO_4 peaks became minor phases, which can correlate with JCPDS file number 03-0726 [14], 06-0399 [15] and 24-0130 [16] respectively. After calcination at 1250°C, the peaks corresponding to BaTiO_3 , BaZrO_3 and Ba_2ZrO_4 were not detectable. Evidently, a single phase of BZT is formed by calcination at 1300°C. The strongest reflections in the majority of the XRD patterns can be identified as the perovskite phase of the composition $\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$, which can be matched with the JCPDS file number 36-0019 [17]. To a first approximation, this phase is a cubic perovskite type structure.

The percentage of the perovskite phase of BZT powders as a function of calcination temperatures was calculated. The perovskite phase of 800 to 1250°C calcined samples did not reach a hundred percent. The single phase of perovskite of the calcined samples at a temperature higher than 1300°C was formed. The percentage of the BZT perovskite phase was increased with increasing of calcination temperatures listed in Table 1.

SEM photographs of BZT powders calcined between 800 and 1350°C are shown in Fig. 2. These powders exhibit an almost spherical morphology and have a porous agglomerated form. As the temperature increased, more agglomerate particles could be observed.

The average particle size tended to increase as calcination temperatures increased as shown in Table 1.

The BZT powders, calcined at 1300°C, were pressed into pellets and sintered at various temperatures. The XRD patterns of sintered ceramics are plotted in Fig. 3. It confirms that all samples were free of minor phase peaks. BZT ceramics are identified as a single phase with a perovskite structure which has a cubic symmetry, as reported in previous investigations [18].

Microstructure developments of sintered pellets were investigated by SEM. The surface of BZT ceramics at various sintering temperatures from 1450 to 1600°C are shown in Fig. 4. The average grain sizes increased from 3.9 to 25.1 μm (Table 1) with increasing of sintering temperature from 1400°C to 1600°C and the results also show a nonuniform distribution of grain size. These results agreed with previous work [11].

The maximum of dielectric constant ($\epsilon_{r,\text{max}}$) increased from 3600 to 5800 as the sintering temperature increased from 1400 to 1550°C. A further increase in the sintering temperature to 1600°C results in a drop in the values of $\epsilon_{r,\text{max}}$ to 4300 as shown in Fig. 5. In the sintering temperature range of 1400 to 1550°C, the density increases with increasing sintering temperature. Further increase in the temperature to 1600°C leads to the decrease of the density (Figure 5). This feature creates a maximum density value of 98.3 % of theoretical density which is comparable to the value of JCPDS file No. 36-0019. The maximum dielectric constant corresponded with the density. The Curie temperature (T_c) of BZT ceramics are shown in Table 1. The T_c of BZT ceramics sintered between 1400 and 1550°C were about -63°C . While, the T_c of BZT ceramics sintered at 1600°C dropped to -92°C . These results suggested that the optimum sintering temperature of BZT ceramics is 1550°C. The decrease in $\epsilon_{r,\text{max}}$, density and T_c of 1600°C sintered ceramic indicated that the composition of BZT was changed with a high sintering temperature.

Conclusion

$\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ powders can be formed through the reaction of barium carbonate, titanium (IV) oxide and zirconium (IV) oxide via calcined temperature at 1300°C. The resulting BZT powders were more agglomerated as the calcination temperature increased. BZT ceramic was identified by XRD as a single phase with the perovskite structure having cubic symmetry and the effect of sintering temperature on the densification, average grain size and dielectric properties was investigated. High density and dielectric constant of BZT ceramics were obtained for the sintering temperature about 1550°C.

Acknowledgment

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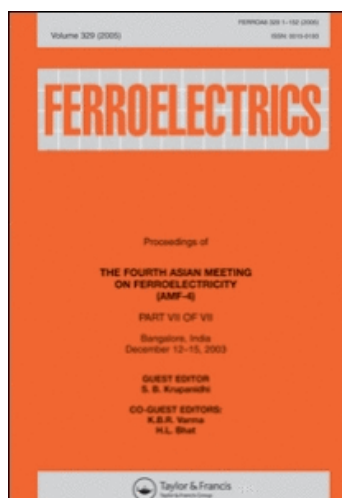
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The Influence of Calcination Temperature on Phase and Morphology of $\text{Ba}(\text{Sn}_{0.05}\text{Ti}_{0.95})\text{O}_3$ Powders Synthesized via Solid State Reaction Method and Combustion Technique

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The Influence of Calcination Temperature on Phase and Morphology of $\text{Ba}(\text{Sn}_{0.05}\text{Ti}_{0.95})\text{O}_3$ Powders Synthesized via Solid State Reaction Method and Combustion Technique

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Barium stannate titanate [$\text{Ba}(\text{Sn}_{0.05}\text{Ti}_{0.95})\text{O}_3$; BST5] powders were synthesized via a solid state reaction and combustion techniques. The single perovskite phase of BST5 powders was found with calcinations temperature of 1200°C for both techniques. The percent of perovskite and lattice parameter a increased with an increase of calcinations temperature. The average particle size increased from 0.54 to 0.86 μm for the solid state reaction method and 0.35 to 0.78 μm for the combustion technique when increasing calcinations temperature from 600 to 1200°C. The average particle size from the combustion technique was smaller than the solid state reaction method.

Keywords Solid state reaction method; combustion technique; morphology; phase formation

Introduction

Barium Stannate Titanate [$\text{Ba}(\text{Sn}_{1-x}\text{Ti}_x)\text{O}_3$; BST] is a binary solid state system composed of ferroelectric barium titanate and non-ferroelectric barium stannate [1]. This material was one of earliest prototypes for a diffused phase transition study. The crystallographic phase structure evolves from tetragonal, to orthorhombic, to rhombohedral to cubic with an increased tin composition at room temperature [2]. The properties of this material, such as Curie temperature or dielectric maximum of BST, can widely shift by changing the Sn ion content. Moreover, the permittivity is very high and the temperature is bias field sensitive. BST can be used in various applications, such as capacitors, bolometer, actuators [3, 4] and microwave phase shifters [5–7]. A survey of literature has reported that the BST has been successfully prepared via a mix of hydrothermal and solid state reactions. It started from the hydrothermal synthesized BaTiO_3 powders, mixed by ball milled with the raw materials BaCO_3 and SnO_2 , and then calcined at 1000–1100°C for 3 h. The calcined powders were sintered at 1250–1500°C for 2 h [1]. They suggested that this solution system is a mutual soluble and the lattice constant was increased as the Sn content increased [1]. The relaxation behavior of BST ceramics can be observed in the samples with $0.2 \leq x \leq 0.3$ [8].

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It is well known that the mixing of hydrothermal and solid state reaction methods is intricate, and difficult for preparation. The conventional solid state synthetic route is probably one of the most fundamental and practical method which has been used, developed, and modified in the both scientific research and industry mass production for many years [9, 10]. Furthermore, in recent years, many researchers have been interested in the preparation of oxide ceramics by the combustion technique, because of its simplicity, fine and agglomerating free crystalline particles and it can also calcinate at a lower temperature [11]. However, a detailed study of the synthesis and characterization of $[\text{Ba}(\text{Sn}_{0.05}\text{Ti}_{0.95})\text{O}_3$; BST5] powders via solid state reaction and combustion techniques have not been reported yet. Therefore, in the present work, the Influence of calcinations temperature on the phase formation and morphology of barium stannate titanate powders synthesized via solid state reaction and combustion technique were investigated.

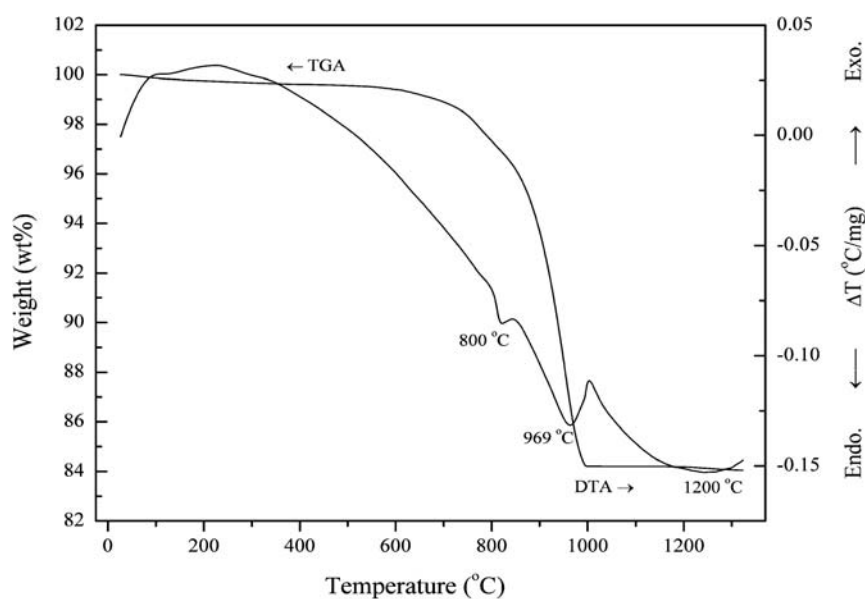
Experimental

The $[\text{Ba}(\text{Sn}_{0.05}\text{Ti}_{0.95})\text{O}_3$; BST5] powders were synthesized via the solid state reaction and combustion techniques. The raw materials of barium carbonate (99%), stannate oxide (99%) and titanium oxide (99%) were weighted in the required stoichiometric ratio and ball-milled in a zirconia milling media under ethanol for 24 hours. The suspensions were dried and the powder ground using an agate mortar and sieved into a fine powder. Then, the mixed powders were calcined with temperatures ranging from 600 to 1200°C for 4 hours. Thermogravimetric and differential thermalanalysis (TGA-DTA) techniques were used to monitor the thermal behavior of the reaction between the oxides precursors in the powdered mixture. The calcined powders were subsequently examined by X-ray diffraction (XRD) to identify the phase formed and optimum calcinations temperature of the BST5 powders. The powders morphologies and particle size were directly imaged by using the scanning electron microscope (SEM). For the combustion technique, the mixture of raw materials and the fuel, urea, in the ratio of 1:2 were well-mixed before the calcination step and the other processes were the same as the solid state reaction method.

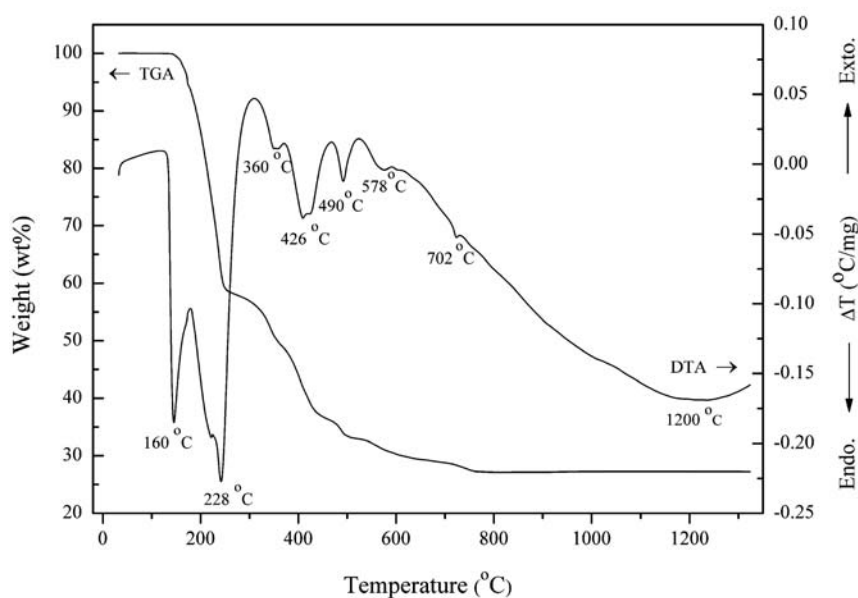
Results and Discussion

The DTA-TGA curves obtained for the stoichiometric properties of BST5 synthesized via a solid state reaction method and combustion technique are shown in Fig. 1(a) and 1(b). In Fig. 1(a) the weight loss, observed above 600°C, corresponded to the chemical reaction of the raw material between BaCO_3 , SnO_2 and TiO_2 . A strong chemical reaction occurred at about 800°C, 969°C and again at 1200°C. Figure 1(b), the TGA curves showed two distinct weight losses. The first weight loss occurred below 300°C, due to the melting of urea and corresponded to the endothermic peak at about 160°C and 228°C. The second one began at 300°C, which can be attributed to the rapid vaporization of water and gas caused by the melting of the urea. This related to the endothermic peak in the DTA curve at 360, 426, 490 and 578°C. The chemical reaction between BaCO_3 , SnO_2 and TiO_2 was obtained and related to the small endothermic peak at 702°C. No abnormality was detected in the TGA curve above 750°C, whilst the reactions were continuous to 1200°C. The endothermic peak at around 1200°C was due to the formation of the BST5 perovskite phase. These data were used to define the range of temperatures for XRD investigation.

The XRD pattern of BST5 powders prepared by a solid state reaction method and a combustion technique are shown in Fig. 2(a) and 2(b). The diffraction synthesis line



(a)



(b)

Figure 1. TGA-DTA curves for the mixture of BST5 powders synthesized via (a) solid state reaction method and (b) combustion technique.

can be indexed on the basis of the cubic structure. The impurity of BaCO_3 , BaO , BaO_2 , SnO , SnO_2 , TiO , TiO_2 , BaSnO_3 , Ba_2TiO_4 and BaTiO_3 were discovered at calcination temperatures below 1200°C in both the solid state reaction and combustion techniques. The pure cubic perovskite phase was found in powders calcined at 1200°C in both the solid state reaction method and combustion technique. This observation agrees with those

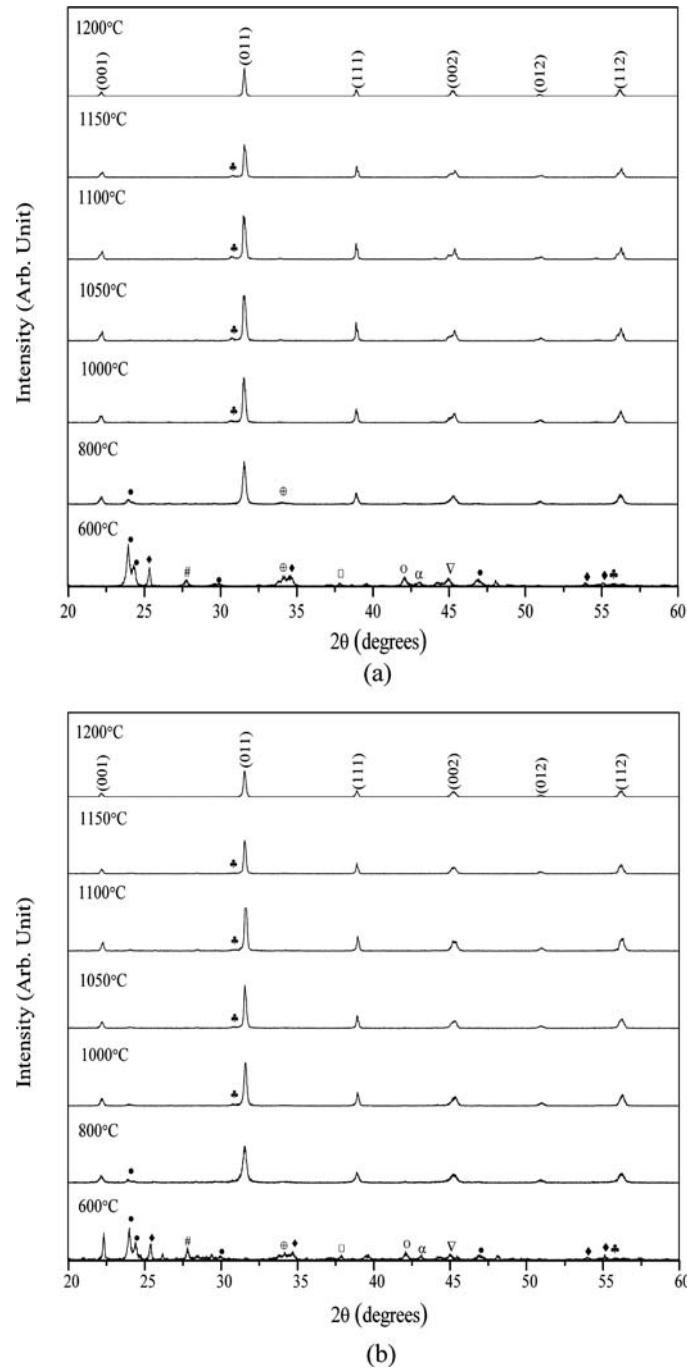
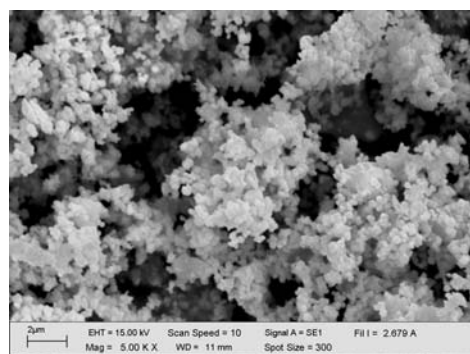


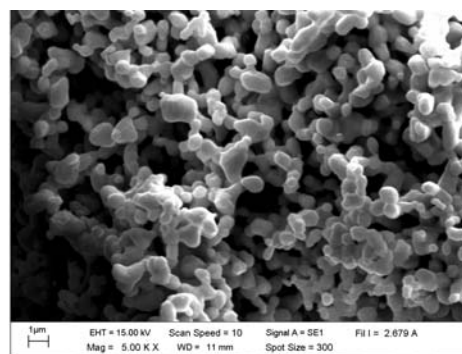
Figure 2. XRD patterns of BST powders prepared by solid state reaction method; (●) $BaCO_3$, (α) BaO_2 , ($\diamond$) TiO_2 , (♣) $BaTiO_3$, (⊕) SnO , (o) TiO , (□) SnO_2 , (φ) $BaSnO_3$, (#) BaO and (∇) Ba_2TiO_4 .

Table 1
Percent perovskite, lattice parameter a and average particle size of BST5

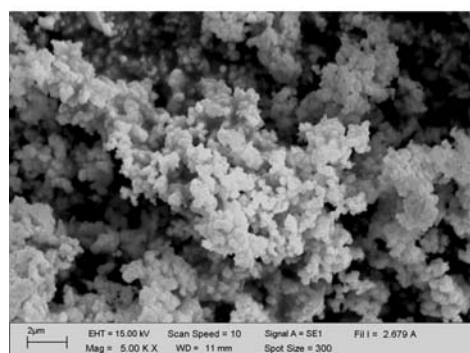
Solid state reaction method				Combustion technique		
Calcined Temperature ($^{\circ}\text{C}$)	Percent perovskite (%)	Lattice parameter a ($\text{\AA}$)	Average particle size (μm)	Percent perovskite (%)	Lattice parameter a ($\text{\AA}$)	Average particle size (μm)
600	34.3	—	0.54	33.7	—	0.35
800	81.5	4.0025	0.59	83.7	3.9983	0.36
1000	84.0	4.0067	0.61	86.2	4.0008	0.39
1050	87.4	4.0069	0.66	91.0	4.0027	0.48
1100	89.6	4.0088	0.68	95.6	4.0068	0.59
1150	94.8	4.0138	0.73	98.5	4.0096	0.69
1200	100	4.0185	0.86	100	4.0117	0.78



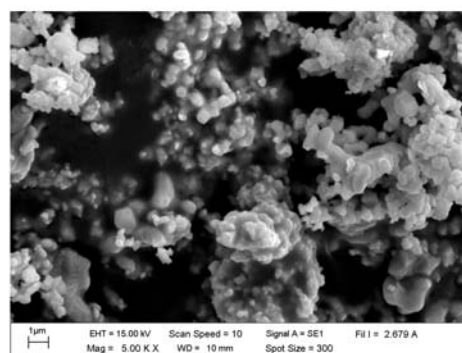
(a)



(b)



(c)



(d)

Figure 3. SEM morphology of BST5 powders (a) calcined at 800°C via solid state reaction method (b) calcined at 1200°C via solid state reaction method (c) calcined at 800°C via combustion technique and (d) calcined at 1200°C via combustion technique.

derived from the DTA-TGA result. The percentage of BST5 perovskite phase increased with an increase of the calcinations temperature, demonstrated in Table 1.

The lattice parameter a tended to increase as calcinations temperature increased: list in table 1. This result indicated that the calcinations temperature is directly affected the crystal structure and the phase formation of BST5 powders.

Figure 3 shows the SEM photographs of BST5 powders synthesized via solid state reaction method and combustion technique. According to the SEM micrographs, the particle sizes were spherical and have a porous agglomerated form. The average particle sizes of BST5 were 0.54–0.86 μm for the solid state reaction method and 0.35–0.78 μm for the combustion technique. Correspondingly, the average particle size of both techniques increased with increased calcinations temperatures, as showed in Table 1. In each calcination temperature, the average particle size via the combustion technique was smaller than with the solid state reaction method.

Conclusions

Barium stannate titanate [$Ba(Sn_{0.05}Ti_{0.95})O_3$; BST5] powders can be synthesized via a solid state reaction method and combustion technique. The pure cubic perovskite phase was obtained with a calcination temperature of 1200°C for both techniques. The average particle size and lattice parameter a increased with increased calcination temperature. The average particle size and lattice parameter prepared from the combustion technique was smaller than with the solid state reaction method. The calcinations temperatures have a strong influence on the crystal structure, lattice parameter and homogeneity of the calcined powders.

Acknowledgments

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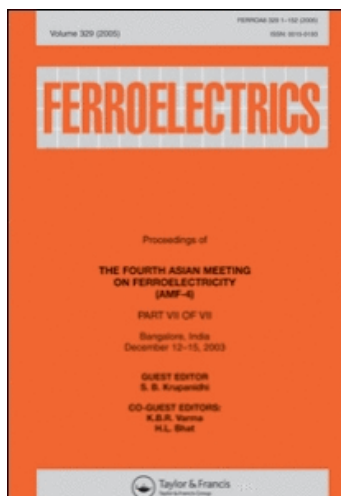
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The Preparation of $\text{Ba}(\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_3$ Ceramics via a Solid State Reaction Method

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The Preparation of $\text{Ba}(\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_3$ Ceramics via a Solid State Reaction Method

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The optimum condition for the preparation of barium stannate titanate $[\text{Ba}(\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_3$; BST10] ceramics by solid state reaction method were studied. BST10 were calcined between 600 and 1200°C for 4 h and sintering temperatures ranged between 1250 and 1450°C for 2 h. It was found that a high purity of perovskite powders was obtained at a calcination temperature of 1200°C. The average particle size and average grain size increased from 0.41 to 0.80 μm and 0.60 to 2.25 μm by increasing the calcined and sintered temperatures. The highest density and dielectric constant were 5.51 g/cm^3 and 529 obtained from the ceramic sintered at 1350°C of sintering temperature.

Keywords Barium stannate titanate; phase formation; microstructure; solid state reaction

Introduction

$\text{Ba}(\text{Sn}_x\text{Ti}_{1-x})\text{O}_3$ is a ferroelectric solid solution which is synthesized by adding Sn ions at the B-site of the BaTiO_3 . The Curie temperature or maximum dielectric constant can be widely shifted by changing the tin content. Due to this, it has been identified as a capacitor, bolometer and actuator [1, 2]. Xiaoyong et al. [3] has revealed that $\text{Ba}(\text{Sn}_x\text{Ti}_{1-x})\text{O}_3$ ceramics with $0 \leq x \leq 1$ prepared by mixed hydrothermal and a solid state reaction method showed a mutual soluble and the lattice constant increased with increased Sn content. The $\text{Ba}(\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_3$: BST10 showed abnormal dielectric properties and a strong electric non-linearity [4]. These make BST10 ceramics interesting for dielectric amplifiers and switching circuit snubbers [5–8].

It is well known that the mixed hydrothermal and solid state reaction method is complicated and difficult. The solid state reaction method is interesting because it is probably one of the most fundamental, practical, routine methods which has been used, developed and modified in both scientific research and industrial mass production for many years [9, 10]. A detailed study of the synthesis and characterization of $\text{Ba}(\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_3$: BST10 ceramics by the solid state reaction method has rarely been reported in the literature. So, in this present work, The $\text{Ba}(\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_3$: BST10 ceramics were prepared by a solid state

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reaction method. The effect of the firing temperature on phase formation, crystal structure and dielectric properties of BST10 ceramics were investigated.

Experimental

Ba(Sn_{0.1}Ti_{0.9})O₃ ceramics were prepared by a solid state reaction method. The raw materials of barium carbonate (BaCO₃), tin oxide (SnO₂) and titanium oxide (TiO₂) were weighted and mixed by ball milling for 24 h in ethanol. After being dried and sieved, the mixture was calcined from 600 to 1200°C for 4 h. The BST10 powders calcined at 1200°C were reground by wet ball milling with 1 wt% binder for 24 h, then were dried and sieved again. The powder mixtures were isostatically pressed into a pellet 15 mm in diameter. The green pellets were sintered from 1250 to 1450°C for 2 h. The thermogravimetric and differential thermal analysis (TGA-DTA) technique was used to monitor the thermal behavior of the reaction between the oxides precursors carried out on the powdered mixture. The phase formation of the calcined powders was analyzed by a X-ray diffractometer (XRD). The microstructures of calcined powders and the sintered samples were examined using scanning electric microscopy (SEM). The density measurement was by Archimedes's method. The dielectric constant at room temperature was also measured by a LCR meter.

Results and Discussion

The TGA-DTA curves, recorded at a heating rate of 10°C/min in air for an equimolar mixture of barium carbonate, stannate oxide and titanium oxide, where the ratio of Sn:Ti is 0.1:0.9, are show in Fig. 1. The TGA curve shows weight loss occurred between 600 and 1000°C, due to the solid state reaction between BaCO₃, SnO₂ and TiO₂. This corresponded to the endothermic peak in the DTA curve at 852 and 953°C. The DTA curve shows a broad

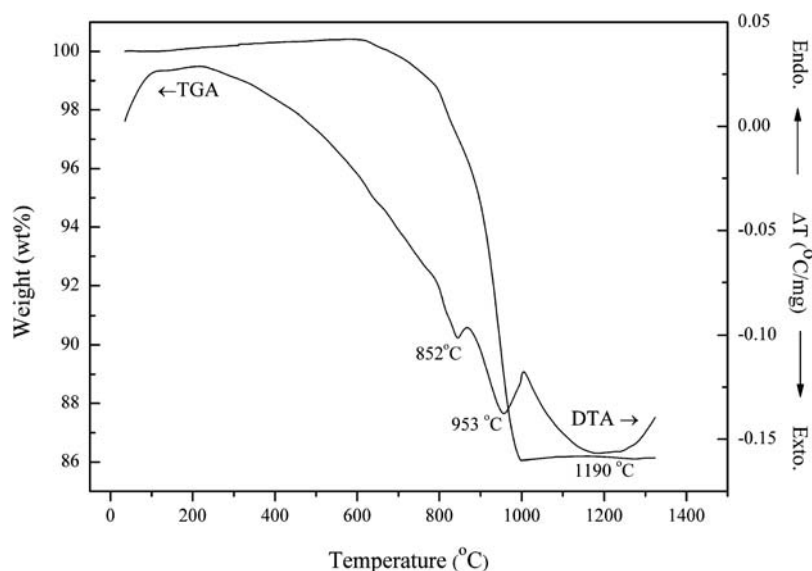


Figure 1. TGA-DTA curves for the mixture of BST10 powders prepared by solide state reaction method.

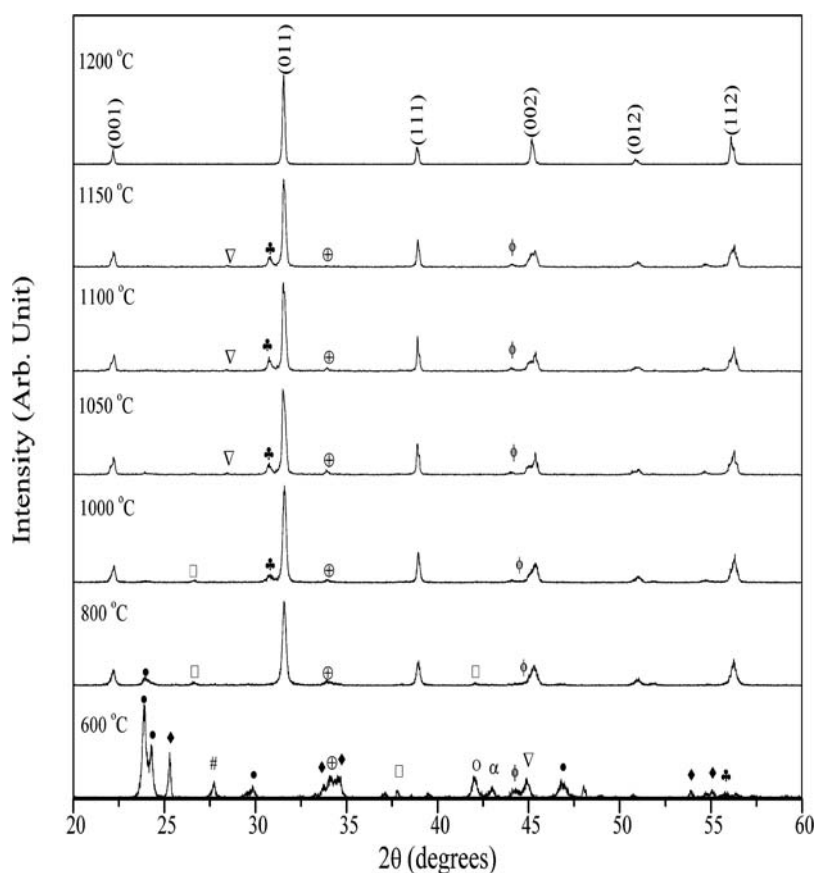


Figure 2. XRD patterns of BST10 powders prepared by solid state reaction method; (•)BaCO₃, (α)BaO₂, (◇)TiO₂, (♣)BaTiO₃, (⊕)SnO, (○)TiO, (□)SnO₂, (φ)BaSnO₃, (#)BaO and (∇)Ba₂TiO₄.

characteristic at around 1190°C. No abnormality was detected in the TGA curve above 1000°C. These data were used to define the range of optimum calcination temperature.

For the XRD pattern of BST10 prepared by a solid state reaction method, calcination temperatures from 600 to 1200°C are shown in Fig. 2. The X-ray analysis indicated that the BST10 calcined at 600°C demonstrated secondary phases of BaCO₃, BaO, BaO₂, SnO, SnO₂, TiO, TiO₂, BaSnO₃, BaTiO₃ and Ba₂TiO₄. At 800°C, the BST10 perovskite phase was formed and the second phases of BaCO₃, SnO, BaSnO₃ and SnO₂ were detected as a separate phase. As the temperature increased to 1000°C the crystalline phase of BST10 was accompanied by SnO, SnO₂, TiO₂, BaSnO₃ and BaTiO₃ phases. Between 1050 and 1150°C, the minor phase of SnO, Ba₂TiO₄, BaSnO₃ and BaTiO₃ remained. At the 1200°C, the pure cubic phase perovskite of the calcined sample was formed. In general, BaTiO₃ is formed at lower than 1200°C [11]. The initial formation of BaTiO₃ starts by the reaction of raw materials BaCO₃ and TiO₂ at the grain boundary. At lower than 1100°C, the reaction progresses, BaTiO₃ and BaCO₃ react to form Ba₂TiO₄ until the BaCO₃ is used up. The remaining TiO₂ then reacts with Ba₂TiO₄ to form BaTiO₃ at lower than 1200°C. Therefore, in this study, BST10 and BaTiO₃ separately formed at lower than 1200°C. XRD investigation matches with data received from the TGA-DTA results. The percentage of

Table 1

Percent perovskite phase, lattice parameter a , average particle size, average grain size, density, shrinkage and dielectric constant of BST10

Calcined powder				Sintered ceramics		
Calcined temperature (°C)	percent perovskite phase (%)	Lattice parameter a (Å)	Average particle size (μm)	Sintering temperature (°C)	Average grain size (μm)	Shrinkage (%)
600	23.0	—	0.41	1250	0.60	7.33
800	83.8	4.0193	0.50	1300	0.71	9.33
1000	85.5	4.0202	0.51	1350	1.22	14.67
1050	88.7	4.0216	0.59	1400	1.62	14.67
1100	91.2	4.0233	0.67	1450	2.25	16.00
1150	94.5	4.0245	0.69			
1200	100	4.0260	0.80			

BST10 perovskite phase increased with increased calcination temperature, demonstrated in Table 1.

The lattice parameter a was calculated and is illustrated in Table 1. The lattice parameter a tended to increase with an increase of calcination temperatures. This indicated the

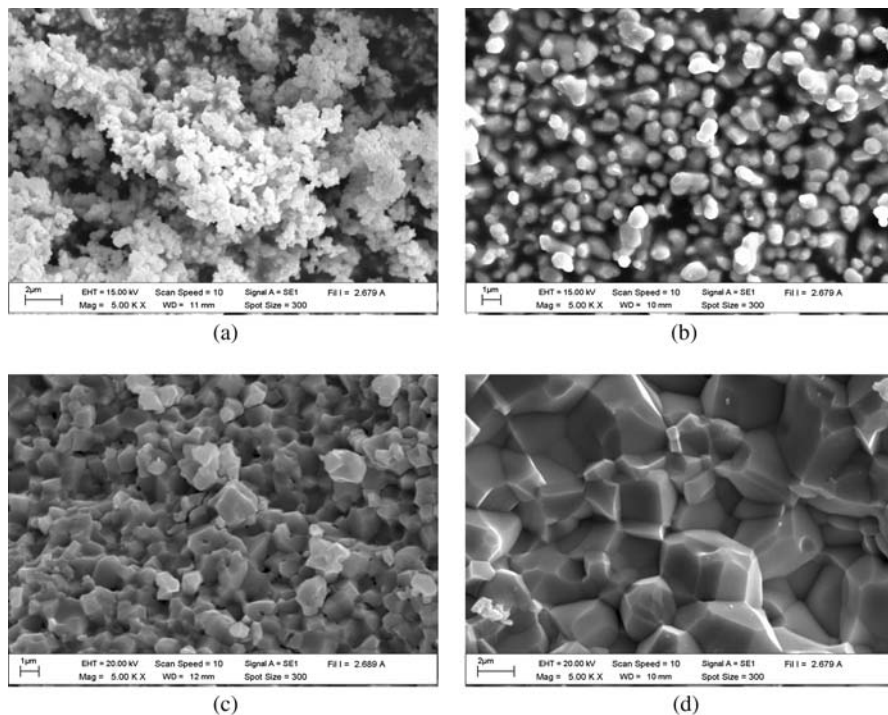


Figure 3. SEM morphology of BST10 (a) powder calcined at 800°C (b) powder calcined at 1200°C (c) ceramic sintered at 1300°C and (d) ceramic sintered at 1450°C.

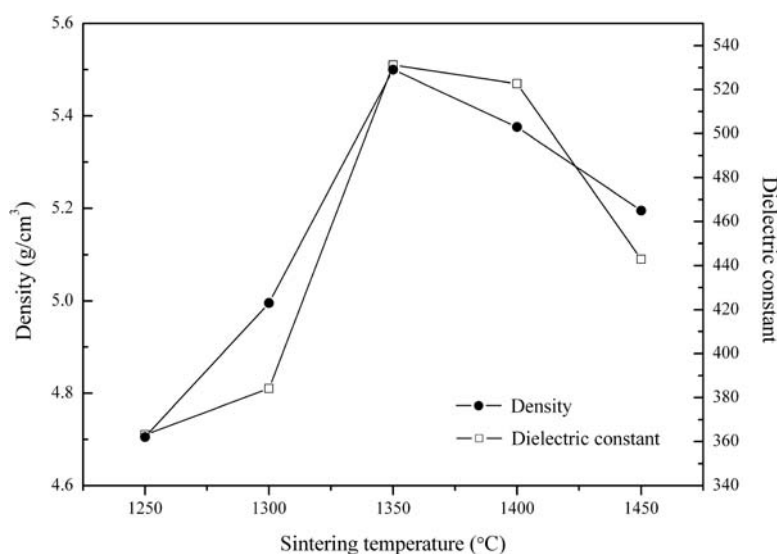


Figure 4. Density and dielectric constant at room temperature of BST10 ceramics.

calcination temperatures have a direct bearing on lattice parameter and unit cell volume. The pure cubic perovskite phase was found in all sintered samples.

SEM photographs of BST10 powders calcined at 800°C and 1200°C for 4 hours are shown in Fig. 3 (a) and (b). The particle sizes are agglomerated and irregular in shape. The average particle size increased from 0.41 to 0.80 μm as calcination temperatures increased from 600 to 1200°C (Table 1). Figure 3 (c) and (d) shows the SEM photographs of BST10 ceramics samples sintered at 1300°C and 1450°C. These photographs show well-developed grain size and dense microstructure. The average grain size increases with increasing sintering temperatures from about 0.60 to 2.25 μm when the sintering temperatures are between 1250 to 1450°C, as shown in Table 1. Moreover, porosity was evidenced in the ceramics sintered at low temperature.

The shrinkage of BST10 ceramics increased when sintering temperature increased as seen in Table 1. The density and dielectric constant at room temperature of BST10 ceramics with different sintering temperatures are shown in Fig. 4. The density and dielectric constant was increased by sintering temperatures up to 1350°C. A further increase in the sintering temperature resulted in a drop of both values. The highest density and dielectric constant were 5.51 g/cm³ and 529 obtained from the ceramic sintered at 1350°C. This result also indicated that the dielectric constant is relative to the density of ceramics.

Conclusions

Barium stannate titanate, BST10 can be prepared by the solid state reaction method and formed by the reaction of barium carbonate, stannium oxide and titanium oxide at 1200°C of calcination temperature. Particle sizes and grain sizes were increased with increased calcination and sintering temperatures. Maximum density and dielectric constant were obtained from the ceramic sintered at 1350°C. These results suggest that the calcination and sintering temperature directly relate to phase formation, microstructure, density and dielectric properties of BST10.

Acknowledgment

This work received financially supported by the Thailand Research Fund (TRF) and Commission on Higher Education (CHE). Thanks also to Department of Physics, Faculty of Science, Naresuan University for supporting facilities. Acknowledgements also to Mr. Don Hindle, for helpful comments and corrections of the manuscript.

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The Effect of Calcination Temperatures on the Phase Formation and Microstructure of $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ Powders

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Keywords: lead strontium titanate, mixed oxide, tetragonality, calcination temperature

ABSTRACT

$(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) ($x=0.25, 0.50$) powders were synthesized by a mixed oxide solid-state reaction method under various calcination temperatures (600-1100°C). Powder samples were characterized using thermogravimetric (TGA), differential thermal analysis (DTA), x-ray diffractometer (XRD) and scanning electron microscopy (SEM). The results showed that a single-phase of PST for $x=0.25$ and 0.50 powders was successfully obtained with a calcination condition of 950 °C for 2 h with a heating/cooling rate of 5°C/min. The TGA-DTA results corresponded to the XRD investigation. The lattice parameter a increased whilst the lattice parameter c decreased with increasing calcination temperatures. The tetragonality of powders decreased with an increase of calcination temperatures. The average particle size of the powders increased with the increase of calcination temperature.

INTRODUCTION

$(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) is a complete solid solution of PbTiO_3 (PT) and SrTiO_3 (ST). The solid solution compounds were indexed in a tetragonal system for $x \leq 0.5$ and in a cubic one for $x \geq 0.5$. The lattice parameters of $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ continuously change but the changing tendency is nonlinear [1]. The Curie temperature of PST is composition-dependent because it can be adjusted from -200 to 490 °C by the ratio of PT and ST [2]. Xing *et al.* [1] demonstrated that the Curie temperature of $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ with $x=0.15, 0.20, 0.5$ was 200 °C, 150 °C and below room temperature. Zhao *et al.* [3] suggested that PST with $x \leq 0.5$ was a promising candidate as positive temperature coefficients of the resistivity (PTCR). Furthermore, due to its large electric field-dependent dielectric constant at a temperature near the Curie temperature, PST is highly suitable for electronic and microelectronic applications, such as microwave devices, frequency tuning devices, capacitors, sensors, etc [4-6].

$(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ were prepared by various techniques, such as hydrothermal reaction, coprecipitation method, molten salt preparation, solvothermal synthesis, polymerized complex and emulsion technique [7]. Almost all of these methods use high-purity inorganic or organic chemicals with homogeneity and precise composition as the starting materials, but the production costs are high with little quantity synthesized. The conventional mixed oxide solid-state reaction is more economical for large batch processing of these ferroelectric materials [8]. However, the result of calcining conditions on phase formation and microstructure of the PST powders with $x=0.25$ and 0.50 has not been reported in previous work. Thus, this study investigated the effects of calcining conditions on the crystal structure and morphology evolution of PST powders with $x=0.25$ and 0.50 synthesized by the mixed oxide solid-state reaction method.

EXPERIMENTAL PROCEDURE

$(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) ($x=0.25, 0.50$) was fabricated by the mixed oxide solid-state reaction method using PbO , SrCO_3 and TiO_2 powders 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 100 – 120 °C for 6 h. After being dried and sieved, the powder mixture was calcined from 600 to 1100 °C for 2 h. The reactions of the uncalcined PST powders with $x=0.25$ and 0.50 taking place during heat treatment were investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The calcined powders were subsequently examined by room temperature X-ray diffraction

(XRD) using CuK α radiation to identify the phases formed and optimum calcination condition for the formation of PST powders with $x=0.25$ and 0.50 . Powder morphology and grain size were directly imaged using scanning electron microscopy (SEM).

RESULTS & DISCUSSION

The DTA-TGA simultaneous analysis of the powders mixed in a stoichiometric proportion of PST with $x=0.25$ and 0.50 is displayed in Fig. 1(a) and 1(b). Fig. 1(a), the TGA curve of PST with $x=0.25$ shows two distinct weight losses. The first weight loss occurred at 277°C , which can be attributed to the decomposition of the organic species from the milling process and related to a small

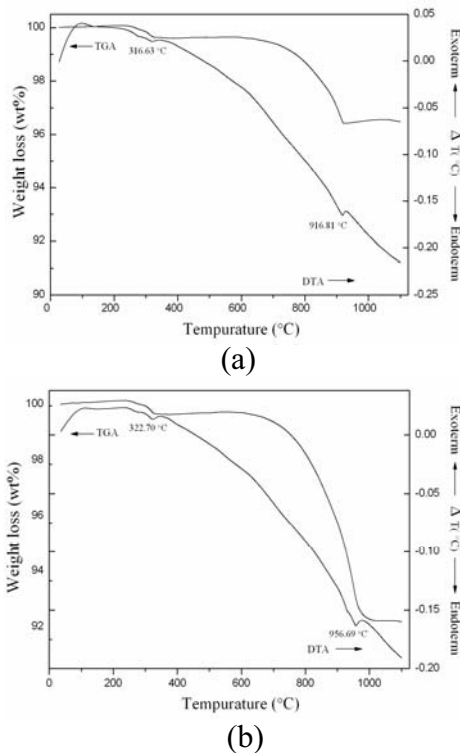


Fig. 1 DTA-TGA curves for the mixture of PbO , SrCO_3 and TiO_2 powders: (a) $x = 0.25$ and (b) $x = 0.50$.

endothermic peak at 317°C in the DTA curve. The second weight loss was observed above 803°C , which corresponded to the endothermic peak at 916°C on the DTA curve. Previous works reported that synthesizing pure PbTiO_3 is based on the solid-state reaction between PbO and TiO_2 , typically at temperatures higher than 630°C [9] while pure perovskite of SrTiO_3 is produced by the solid-state reaction between SrCO_3 and TiO_2 at high temperatures above 1000°C [10]. Therefore, for PST with $x=0.25$, the reaction between PbO , SrCO_3 and TiO_2 should begin at a temperature higher than 800°C and be completely finished at temperatures higher than 920°C . Fig. 1(b), the DTA-TGA trace of PST powder with $x=0.50$, showed similar exothermic and endothermic results as Fig. 1(a). The first weight loss was found at 289°C , and was caused by the decomposition of organic species from the milling process and related to a small endothermic peak at 322°C in the DTA curve. The second weight loss began at 840°C , due to the chemical reaction of raw materials and related to the endothermic peak at 957°C in the DTA curve. These data were used to define the range of calcination temperatures.

XRD patterns of PST powders with $x=0.25$ and 0.50 calcined at $600 - 1100^\circ\text{C}$ are shown in Fig. 2(a) and (b). For powders with $x=0.25$ and 0.50 calcined below 950°C , X-ray peaks of raw materials and impurity such as PbO , SrCO_3 , TiO_2 and TiO appeared. A high purity of the tetragonal perovskite phase was discovered in powders calcined above 950°C . These could be matched with JCPDS file number 06-0452 [11]. The

percent perovskite phase of PST powders with $x=0.25$ and 0.50 are calculated from formula (1) and listed in Table 1. The purity of the perovskite phase rose with increasing temperatures and a hundred percent of the perovskite phase was found above the calcination temperature of 950°C .

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{PbO}} + I_{\text{SrCO}_3} + I_{\text{TiO}_2} + I_{\text{TiO}}} \right) \times 100 \quad (1)$$

This well-known equation is widely employed in connection with the preparation of complex perovskite structure materials. I_{perov} , I_{PbO} , I_{SrCO_3} , I_{TiO_2} and I_{TiO} referred to the intensity of the (101) perovskite peak, intensities of the highest PbO , SrCO_3 , TiO_2 and TiO peaks, respectively.

The a - and c -axis lattice constants of PST powders with $x=0.25$ and 0.50 were calculated from the (001)/(100) and (002)/(200) XRD peaks and are demonstrated in Fig. 3(a) and (b). With an increase of the calcined temperature, the a axis parameter tended to increase, whereas the c axis parameter decreased greatly. The c/a ratio and unit cell volume of PST decreased with increasing calcined temperatures as shown in Table 1. This indicated that the tetragonality decreased gradually to a cubic or pseudo-cubic structure when the calcination temperatures increased. Moreover, at the same calcination temperature, the c/a ratio and unit cell volume of PST powders with $x=0.5$ were lower than $x=0.25$ in every calcined temperature. The lattice contraction was due to Pb being replaced by Sr with a smaller ionic radius [12]. Furthermore, Kim and Kim [13] reported that the phase formation PST ceramics

changed from the tetragonal structure to the cubic structure when the stoichiometric composition was $x=0.5$.

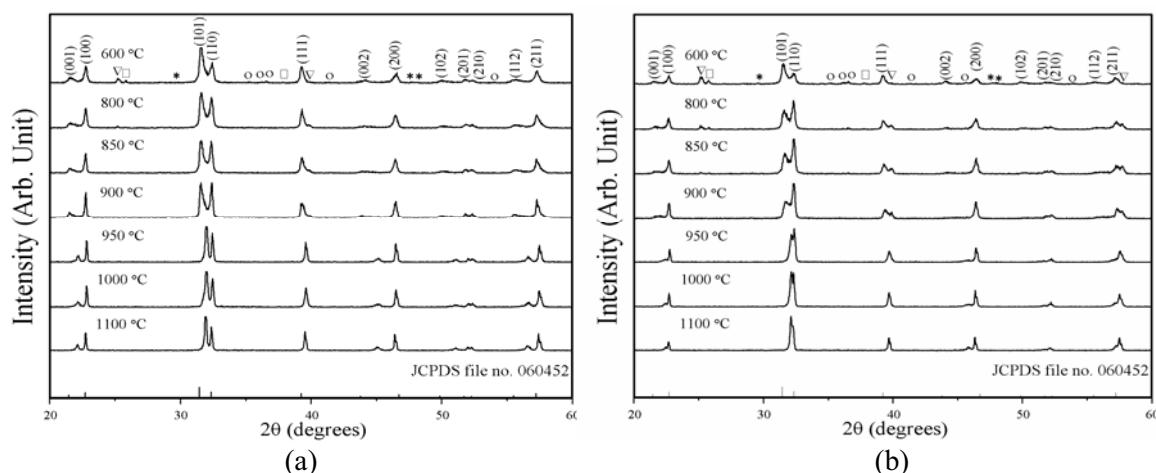


Fig. 2 XRD patterns of the PST calcined powders with (a) $x = 0.25$ and (b) $x = 0.50$ at various temperatures: (* PbO), (∇ SrCO₃), ($\square$ TiO₂) and (o TiO).

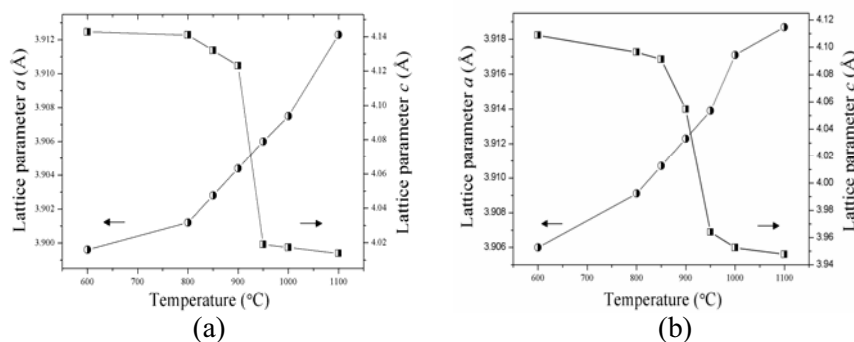
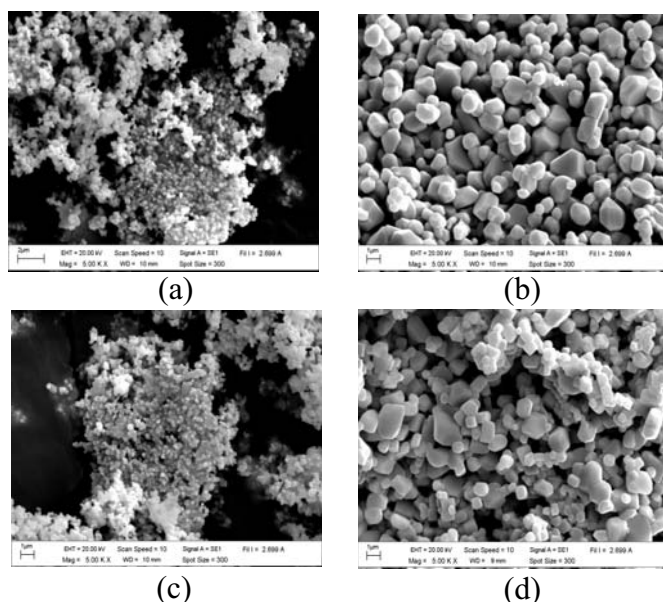


Fig. 3 The lattice parameters a , c of the PST calcined powders at various temperatures: (a) $x=0.25$ and (b) $x=0.50$.



SEM micrographs of PST calcined powders with $x=0.25$ and 0.50 are shown in Fig. 4. These powders exhibited an almost spherical morphology. In general, the particles are highly agglomerated and basically irregular in shape, with a substantial variation in particle size. With an increase of calcination temperatures, the average particle size increased. The results also indicated that the degree of agglomeration tended to increase with increasing calcination temperature. The average particle size of PST powders with $x = 0.25$ and 0.50 was in the range of $0.31\text{--}1.44\text{ }\mu\text{m}$ and $0.30\text{--}1.09\text{ }\mu\text{m}$, respectively.

Fig. 4 SEM Photographs of the PST powders with $x=0.25$ calcined at (a) $600\text{ }^{\circ}\text{C}$ (b) $1100\text{ }^{\circ}\text{C}$ and the PST powders with $x=0.50$ calcined at (c) $600\text{ }^{\circ}\text{C}$ (d) $1100\text{ }^{\circ}\text{C}$.

Table 1. Percent perovskite phase, c/a ratio, unit cell volume and average particle size of the PST powders

x	Calcination temperature (°C)	% perovskite phase	c/a ratio	Unit cell volume (Å ³)	Particle size (μm)
0.25	600	72	1.062	63.0	0.31
	800	79	1.061	63.0	0.48
	850	88	1.058	62.9	0.57
	900	93	1.056	62.8	0.63
	950	100	1.028	61.3	1.03
	1000	100	1.028	61.3	1.24
	1100	100	1.025	61.4	1.44
0.50	600	25	1.051	62.6	0.30
	800	51	1.047	62.5	0.47
	850	65	1.046	62.5	0.55
	900	72	1.036	62.0	0.62
	950	100	1.012	60.7	0.77
	1000	100	1.009	60.6	0.81
	1100	100	1.007	60.6	1.09

CONCLUSIONS

Calcination temperatures have a strong influence on the crystal structure, microstructure, lattice parameter, tetragonality and percentage of the perovskite phase of calcined powders in both compositions. The pure perovskite phase has been discovered when calcination temperatures are above 950 °C. The lattice parameter c decreases, while the lattice parameter a increases with increasing calcined temperatures. The lattice anisotropy (c/a) decreases with increasing calcined temperatures. The particles have a spherical form and tend to extend with the augmentation of temperatures.

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Influences of Firing Temperatures on Phase and Morphology Evolution of $(\text{Ba}_{0.25}\text{Sr}_{0.75})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$ Ceramics Synthesized via Solid-State Reaction Method

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Keywords: Cubic Perovskite Phase, Microstructure, Solid-State Reaction, Nanosized particles

ABSTRACT

The effect of calcination (1000-1400 °C) and sintering temperatures (1400-1600 °C) on the phase formation and microstructure of barium strontium zirconate titanate $[(\text{Ba}_{0.25}\text{Sr}_{0.75})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3]$; BSZT] ceramics were investigated. BSZT powders were prepared by the solid-state reaction method. Higher calcination temperatures increased the percentage of the perovskite phase, but decreased the lattice parameter a of BSZT powders. The pure perovskite phase of BSZT powders was detected above the calcination temperature of 1350 °C. The microstructure of BSZT powders exhibited an almost-spherical morphology and had a porous agglomerated form. The average particle size and the average grain size of the ceramics were increased with the increase of calcination and sintering temperatures. The highest density of the samples was 5.42 g/cm³ which was obtained from ceramic sintered at 1550 °C for 2 h.

INTRODUCTION

A solid solution of barium titanate and strontium zirconate; $(1-x)\text{BaTiO}_3-x\text{SrZrO}_3$ exists in a single phase for wide range of compositions. The solid solution exhibited paraelectric properties, was chemically more stable, had a lower transition temperature (T_c) and had a high dielectric constant ϵ for x value above 0.2 [1]. $(1-x)\text{BaTiO}_3-x\text{SrZrO}_3$ compounds have been applied in microwave dielectric resonators which are miniature resonating devices used in microwave integrated circuits [2]. The tunability and figure of merit of $(\text{Ba}_{0.75}\text{Sr}_{0.25})(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ thin films prepared by pulsed laser deposition are 53% and 38 respectively and were promising candidates for microwave tunable devices [1,3]. A literature survey has revealed that the sol-gel technique reaction has been used for preparing $(1-x)\text{BaTiO}_3-x\text{SrZrO}_3$ powders [4-6]. It is well known that this processing of sample preparation is complex and expensive [7]. The solid-state reaction is probably one of the most fundamental, practical and routine methods which has been used, developed and modified in both scientific research and industrial mass production for many years [8,9]. However, a detailed study of the synthesis and characterization of $(\text{Ba}_{0.25}\text{Sr}_{0.75})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$ ceramics by the solid-state reaction has not been reported in the literature. So, in this present work, the $(\text{Ba}_{0.25}\text{Sr}_{0.75})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$: BSZT ceramics were prepared via solid-state reaction. The effect of calcination and sintering temperatures on the phase formation and microstructure of BSZT ceramics were also investigated.

EXPERIMENTAL PROCEDURE

The starting materials were commercially available: BaCO_3 (99%), SrCO_3 (99%), ZrO_2 (99%) and TiO_2 (99%). Barium strontium zirconate titanate $(\text{Ba}_{0.25}\text{Sr}_{0.75})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$ powder was prepared via the solid-state reaction method by thoroughly grounding mixtures of raw materials by a ball milling procedure (zirconia milling media under ethanol for 24 h). Drying was carried out at 120 °C for 4 h. After sieving, the uncalcined powders were calcined in temperatures ranging from 1000 to 1400 °C, with a dwell time of 4 h and a heating/cooling rate of 5 °C/min. The calcined powders were then pressed into disks with a diameter of 15 mm at a pressure of 80 MPa. The pellets were sintered from 1400 to 1600 °C for 2 h and cooled in a furnace. X-ray diffraction was employed to identify the phase formed and the optimum temperature of the BSZT powders and ceramics. The

calcined powders and sintered ceramics morphologies were imaged using scanning electron microscopy. The density of the sintered ceramics was measured by the Archimedes method. The average particle size and the average grain size were determined by using a mean linear intercept method. The dielectric measurements were carried out at 1 kHz using a LCD meter (Agilent 4263B) at room temperature. The dielectric constant (ϵ_r) was calculated using the geometric area and thickness of the discs.

RESULTS & DISCUSSION

XRD patterns of BSZT powders at different calcination temperatures are shown in Fig.1. The diffraction lines were indexed on the basis of a cubic structure matched with JCPDS file number 03-0632. The impurity phases of BaO, BaTiO₃, TiO₂, ZrO₂ and SrTiO₃ were discovered at calcination temperatures below 1350 °C. The pure cubic perovskite phase was found in powders calcined higher than 1350 °C. The relative amounts of perovskite phase were determined via measuring the major XRD peak intensities of the perovskite phase. The percentage of perovskite phase was emitted by the following equation:

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{BaO}} + I_{\text{BaTiO}_3} + I_{\text{TiO}_2} + I_{\text{ZrO}_2} + I_{\text{SrTiO}_3}} \right) \times 100 \quad (1)$$

This equation is a well-know equation widely employed in connection with the preparation of complex perovskite structure materials [10,11]. Here I_{perov} , I_{BaO} , I_{BaTiO_3} , I_{TiO_2} , I_{ZrO_2} and I_{SrTiO_3} refer to the intensity of the (110) perovskite peak, intensities of the highest BaO, BaTiO₃, TiO₂, ZrO₂ and SrTiO₃ peaks, respectively. The percent perovskite phase of BSZT calcined powders at calcination temperatures ranging from 1000 to 1400 °C for 4 h is shown in Table 1. The increase of phase purity with increasing calcination temperature was evident.

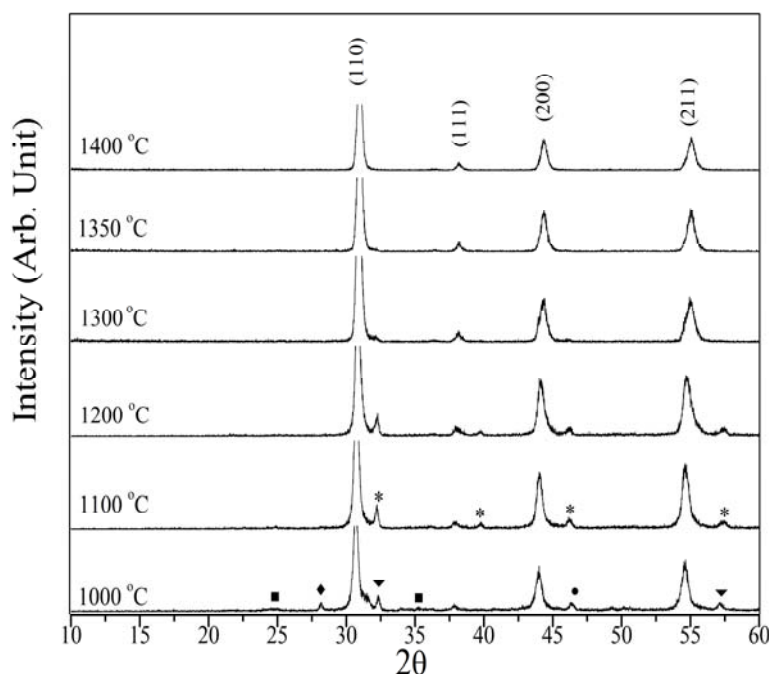


Fig. 1 XRD patterns of BSZT powders calcined at various temperatures for 4 h: (♦)BaO; (●)BaTiO₃; (■)TiO₂; (▼) ZrO₂; (*) SrTiO₃.

The lattice parameter a decreased with increasing calcination temperatures, seen in table 1. The changing of calcination temperatures affected the lattice strain, which is determined as the change in the d spacing and the lattice parameter of the samples [12]. This indicated that the calcination temperatures affected the crystal structure and the phase formation.

Fig.2 (a) and (b) show the SEM photographs of BSZT powders calcined at 1300 and 1400 °C for 4 h. These powders exhibited an almost spherical morphology and had a porous agglomerated form. The average particle size of BSZT powders were between 182 and 381 nm, when calcined between 1000 and 1400 °C. The average particle size increased as calcination temperatures increased, as shown in table 1.

Table 1. The percent perovskite phase, lattice parameter a and average particle size of BSZT powders

Calcined temperature (°C)	Percent perovskite phase (%)	Lattice parameter a (Å)	Average particle size (nm)
1000	71.5	4.1146	182
1100	73.5	4.1137	195
1200	77.1	4.1128	204
1300	95.3	4.0855	251
1350	100	4.0829	322
1400	100	4.0785	381

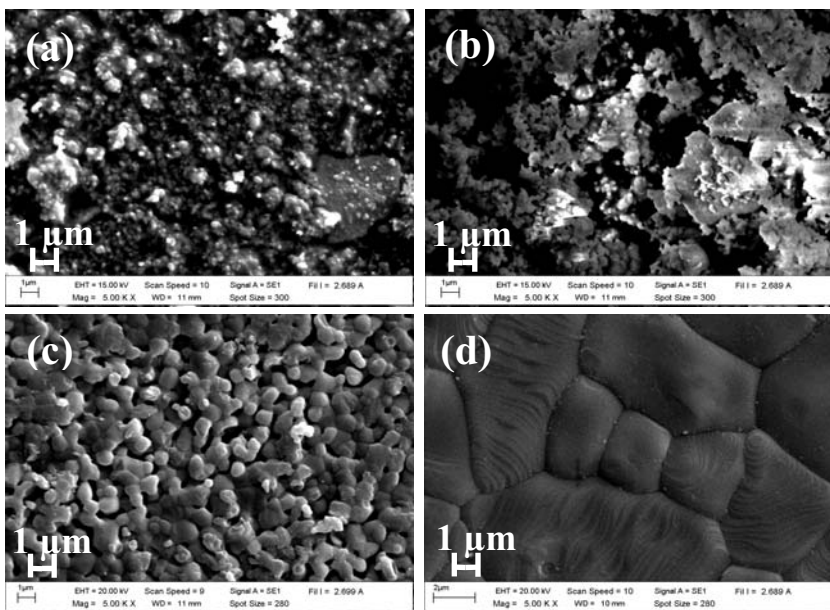


Fig. 2 SEM photomicrographs of the powders calcined at : (a) 1300 °C and (b) 1400 °C, for 4 h and the pellets surface sintered at : (c) 1500 °C and (d) 1600 °C, for 2 h.

The calcined powders obtained at 1350 °C were pressed into pellets and sintered from 1400 to 1600 °C for 2 h. The phase formation behavior of the sintered ceramics was revealed by the XRD method. The BSZT ceramics were identified as a single phase in all samples with a perovskite structure which has a cubic symmetry.

The lattice parameter a as a function of sintering temperatures in this study is shown in Table 2. The lattice parameter a decreased with the increasing of sintering temperatures. The decrease of lattice parameter a may be caused by the changing of the lattice strain which was similar in the calcined powders. This indicated

that sintering temperatures have a direct significance on the lattice parameter.

The SEM photographs of the BSZT surface of the sintered ceramics are shown in Fig. 2 (c) and (d). It was evident that the porosity decreased with the increase of the sintering temperature. The average grain sizes of the BSZT ceramics increased from 0.88 to 2.60 μm when the sintering temperatures increased from 1400 to 1600 °C as shown in Table 2.

The measured density, shrinkage and dielectric constant at room temperature with a variation in the sintering temperatures are shown in Table 2. It can be seen that the density and dielectric constant were first increased by sintering temperatures, reached a maximum at 1550 °C and then dropped in value when the sintering temperature was higher than 1550 °C. The highest density of this work was 5.42 g/cm³ and the highest dielectric constant was 93 which was sintered at 1550 °C for 2 h. These results indicated that the dielectric constant is relative to the density of the ceramic. The percent shrinkage of the pellet samples increased with the increase of sintering temperatures as is shown in Table 2.

Table 2. The lattice parameter a , density, shrinkage, average grain size and dielectric constant at room temperature of BSZT ceramics

Sintered temperature (°C)	Lattice parameter a (Å)	Density (g/ cm ³)	Shrinkage (%)	Average grain size (μm)	Dielectric constant (ϵ_r)
1400	4.0811	5.38	5.13	0.88	59
1450	4.0811	5.39	5.49	1.24	65
1500	4.0785	5.41	10.39	1.45	79
1550	4.0759	5.42	16.95	1.64	93
1600	4.0682	5.41	17.68	2.60	79

CONCLUSIONS

(Ba_{0.25}Sr_{0.75})(Zr_{0.75}Ti_{0.25})O₃ powders can be obtained from a solid-state reaction method. The pure cubic perovskite phase was obtained with a calcination temperature of 1350 °C. The resulting BSZT powders became more agglomerated as the calcination temperature increased. A maximum density of 5.42 g/ cm³ and maximum dielectric constant of 93 were obtained from the ceramic sintered at 1550 °C for 2 h. The calcination and sintering temperatures have a strong influence on the crystal structure, lattice parameter and homogeneity of the calcined powders and the sintered ceramics.

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EFFECT OF SINTERING TEMPERATURE ON THE CRYSTAL STRUCTURE, MICROSTRUCTURE AND PHASE TRANSITION OF $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ CERAMICS

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Polycrystalline $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) ($x = 0.25, 0.50$) ceramics were synthesized by the solid-state reaction method. PST sintering temperatures ranged between 1050–1250°C. The samples were characterized by X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The sintered pellets showed pure perovskite in all samples. The lattice parameter c increased, while the lattice parameter a decreased with increasing sintering temperatures. The tetragonality and average grain sizes increased when sintering temperatures were increased. The dielectric constants vs temperature curves of PST ceramics with $x = 0.25$ and $x = 0.50$ associated with the ferroelectric to paraelectric phase transition, showed a maximum peak at around 311 and 139°C, respectively. The dielectric constants of both compositions were related with their densities.

Keywords: Lead strontium titanate; tetragonality; sintering temperature; crystal structure; microstructure.

Lead strontium titanate $(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ (PST) is currently being investigated as a potential candidate material for future tunable microwave device components (such as resonators, filters, etc.) and for ultra-large scale integration dynamic random access memory (DRAM) capacitors.¹ PST is a ferroelectric solid solution between PbTiO_3 and SrTiO_3 with a tetragonal or cubic structure and has physical properties which vary depending on its composition.² Zhang *et al.*³ reported that the phase transition from the tetragonal structure of pure PbTiO_3 to the cubic structure of SrTiO_3 occurred at the stoichiometric composition of $(\text{Pb}_{0.50}\text{Sr}_{0.50})\text{TiO}_3$. The phase diagram of a PST solid solution was studied by Nomura and Sawada⁴ and recently, in Sr rich samples by Lemanov *et al.*⁵ It was found that the Curie temperature decreased linearly with the increase of Sr content. The pure phase PST has a very high relative permittivity in the desirable application temperature range. For example, a PST film with a Pb/Sr ratio of 40/60 reported by Kim *et al.*^{6,7} has a dielectric constant and tunability of 335 at 100 kHz and 47.89% at 250 kV/cm, respectively.

$(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3$ was prepared by various techniques, such as the sol–gel method,^{8–10} soft chemical process,¹¹ co-precipitation method,¹² and complex polymerization

method.¹³ Almost all of these methods use high purity inorganic or organic chemicals with homogeneity and precise composition as the starting materials but the production costs are high with little quantity synthesized. The conventional solid-state reaction method is more economical for large batch processing of these ferroelectric materials.¹⁴ However, the effect of sintering temperature on the PST ceramics prepared via the solid-state reaction method had not been observed yet. Therefore, investigating the effects of sintering conditions on the crystal structure, microstructure and phase transition of PST ceramics with $x = 0.25$ and 0.50 (henceforth called as PST25 and PST50, respectively) synthesized by the solid-state reaction method was studied in this work.

PST (PST25 and PST50) ceramics were prepared by a conventional solid-state reaction of lead oxide (99% PbO), strontium carbonate (98+% SrCO_3) and titanium oxide (99% TiO_2). The raw materials were ball milled with stabilized zirconia balls and ethanol for 24 h, and then calcined at 950°C for 2 h¹⁵ and sintered at 1050–1250°C for 3 h. The crystalline phase structures of the PST were analyzed by X-ray diffraction (XRD) with CuK_α radiation. Scanning electron microscopy (SEM) was used to examine the surface morphologies and cross-sectional micrographs. Lattice parameters c , a and c/a ratio were determined from the (001)/(100) and (002)/(200)

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reflections plane obtained by a calculation based on XRD peaks. The average particle size and average grain size of samples were determined by using the linear interception method. The apparent density of the samples was measured by the Archimedes method. Dielectric measurements were performed using an LCR meter (Agilent 4263B), and the measuring frequency was 1 kHz.

The XRD patterns of PST25 and PST50 ceramics sintered at various temperatures are shown in Figs. 1(a) and 1(b), respectively. The sintered pellets showed a pure perovskite in both compositions. The diffraction patterns of PST25 and PST50 could be indexed with respect to a tetragonal structure. Our data matched well with JCPDS data file No. 060452¹⁶ and earlier reports.^{17,18} Moreover, it is noted that the (001)/(100) and (002)/(200) peaks are clearly separated in the PST25 pattern. With increasing Sr content from 0.25 mol% to 0.50 mol%, the peaks shifted slightly towards a higher angle. However, there were still a few overlapping peaks in both (001)/(100) and (002)/(200) for the PST50 sintered ceramics, showing a certain degree of tetragonality.

Figure 2(a) shows lattice parameters a , c of PST25 sintered ceramics. The lattice parameter a decreased, while the lattice parameter c increased with an increased sintering temperature. For PST50, the results tend to be similar to PST25. Figure 2(b) shows the c/a ratio of PST25 and PST50 ceramics as a function of sintering temperatures. When the sintering temperature increased from 1050–1250°C, the c/a ratio of PST25 and PST50 was increased from 1.024–1.028 and 1.007–1.010, respectively. Furthermore, at the same sintering

temperature, the c/a ratio of the PST ceramics decreased with an increase of Sr content (from 0.25 mol% to 0.50 mol%). The reduction of the c/a ratio is due to the decrease of the c parameter and the a parameter which remains almost unchanged with the increase in Sr content. It was confirmed that Sr-doped in PT could reduce the tetragonality of PT ceramics.^{4,13}

The SEM photographs of PST sintered ceramics at various temperatures are shown in Fig. 3. It was found that increasing sintering temperatures help grain size grow in both compositions. The average grain size in PST25 and PST50 increased from 0.4 to 1.1 μm and 0.4 to 0.9 μm (Table 1), in agreement with the previous work by Sheng *et al.* and Yimnirun *et al.*^{19,20} A porous microstructure with small grain size is observed in the PST25 sintered at 1050°C. The increase of sintering temperature in this composition significantly promoted the grain growth and microstructural densification. However, the grain size of PST25 sintered above 1150°C also displayed very high degree of porosity. For PST50, very high porosity was observed at low temperature, while good densification and homogenous microstructure were exhibited when the sintering temperature was above 1200°C. Furthermore, the cross-section microstructures of the PST25 displayed predominantly intra-granular cleavage with sintering temperatures above 1150°C. The PST50 ceramic changes from fully inter-granular to fully intra-granular at a sintered temperature of 1250°C. The result indicated that the sintering temperatures strongly affect grain boundaries.

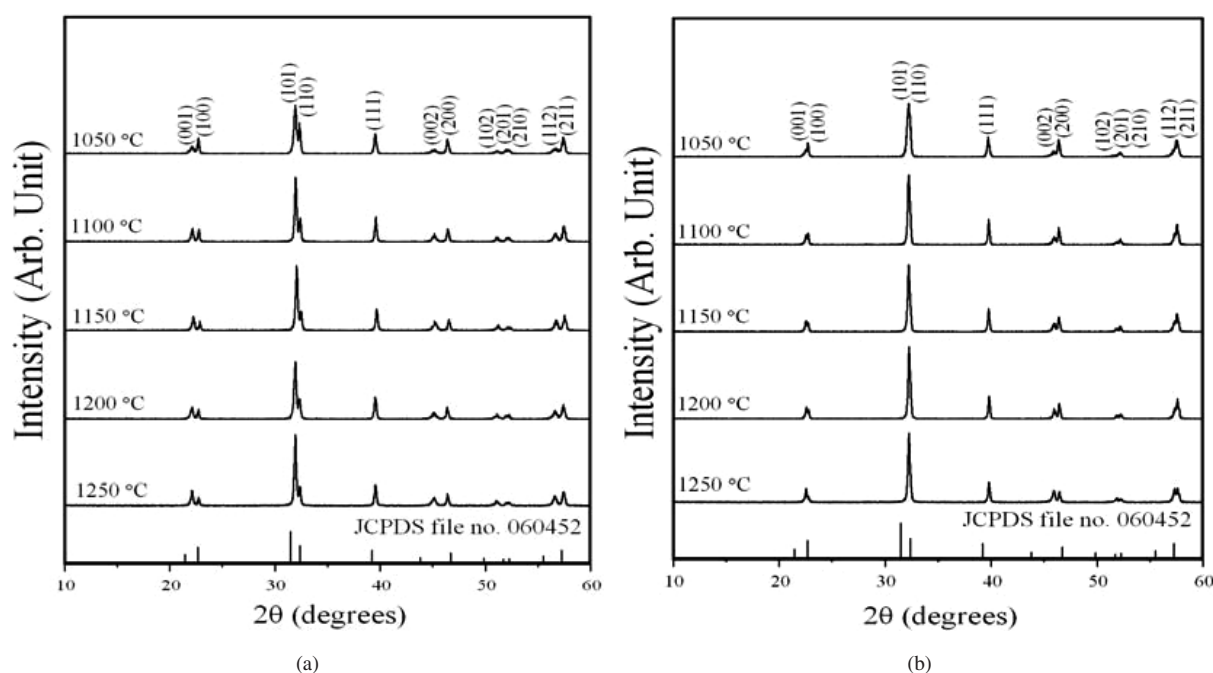


Fig. 1. XRD patterns of the PST sintered ceramics at various temperatures: (a) PST25 and (b) PST50.

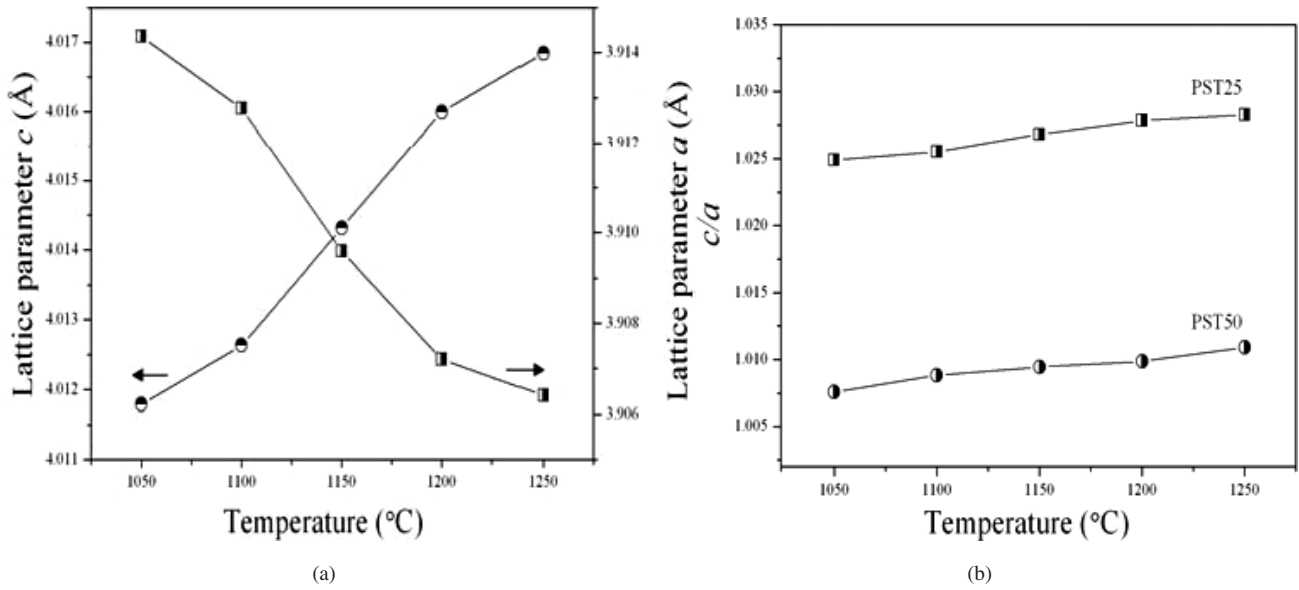


Fig. 2. (a) The lattice parameters a , c of the PST25 sintered ceramics at various temperatures. (b) The lattice anisotropy (c/a) of PST25 and PST50 ceramics as a function of sintering temperature.

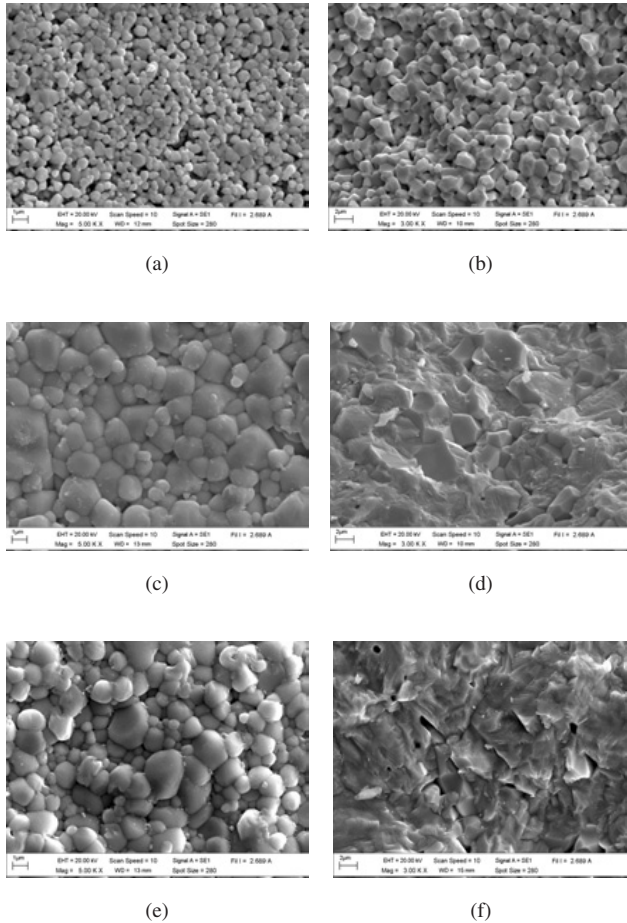


Fig. 3. Surface morphologies and cross-sectional micrographs of the PST25 sintered ceramics: (a) and (b) sintered at 1050°C, (c) and (d) sintered at 1150°C, (e) and (f) sintered at 1250°C.

Table 1. The average grain size, density, shrinkage and dielectric constant of the PST sintered ceramics.

Sintering temperature (°C)	Average grain size (μm)		Density (g/cm^3)		Shrinkage (%)		Dielectric constant at T_c	
	25	50	25	50	25	50	25	50
x								
1050	0.4	0.4	7.19	6.56	7.3	8.0	—	1,300
1100	0.6	0.5	7.40	6.57	13.3	12.6	—	4,000
1150	1.1	0.5	7.66	6.59	15.3	14.0	18,000	5,500
1200	0.8	0.6	7.40	6.60	14.6	14.4	14,200	6,000
1250	1.1	0.9	7.10	6.61	14.6	15.3	13,600	7,900

The density and shrinkage of PST25 and PST50 ceramics with sintering temperatures between 1050–1250°C can be also seen in Table 1. For PST25, the density and shrinkage increased with increasing sintering temperatures from 1050–1150°C, reached a maximum value at 1150°C and decreased after further sintering at a higher temperature (1200°C). The decrease in density of PST25 ceramics sintered at a high temperature (1200°C) may be due to the PbO evaporation, and the presence of a porous microstructure.^{21,22} A similar result was found in $\text{Pb}(\text{Zr}_{0.44}\text{Ti}_{0.56})\text{O}_3$ and $(1-x)\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ - $x\text{BaTiO}_3$ ceramics.^{20,23} For PST50, the density and shrinkage increased with increasing sintering temperatures, and the maximum value was $6.61 \text{ g}/\text{cm}^3$ and 15.3% obtained from sintered at 1250°C, as seen in Table 1. However, when the sintering temperature was over 1250°C, the PST50 ceramics became very fragile.

Figure 4 shows the dielectric constant of PST25 and PST50 sintered ceramics as a function of temperature at

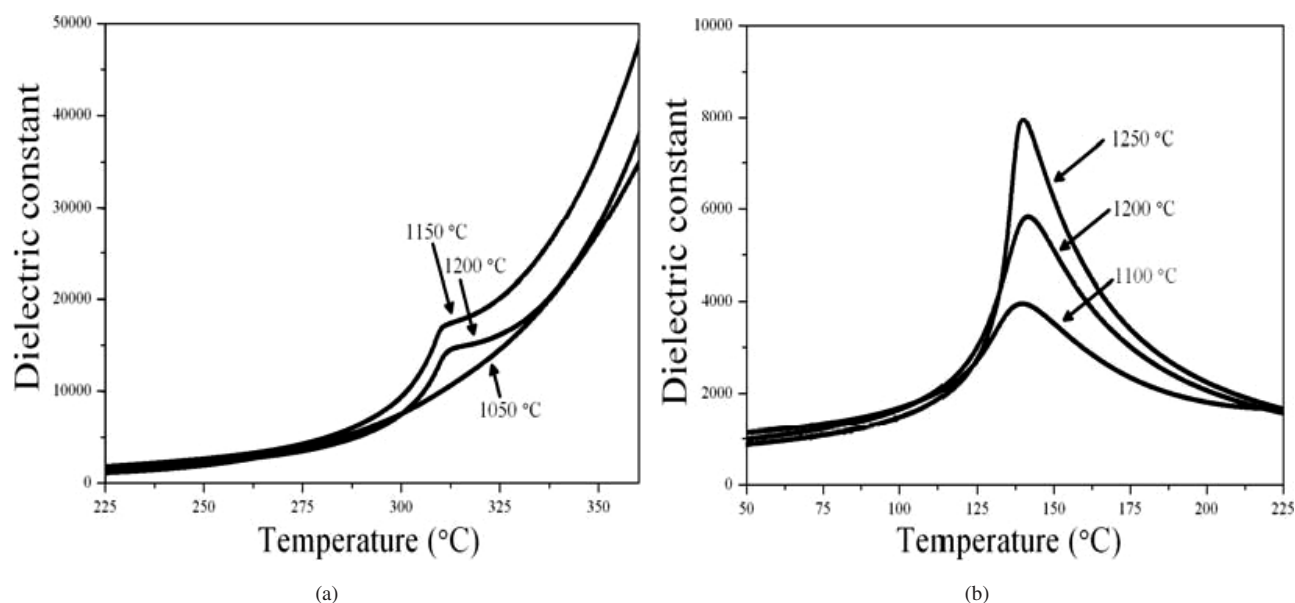


Fig. 4. Dielectric constant of PST ceramics as a function of sintering temperature: (a) PST25 and (b) PST50.

a frequency of 1 kHz. The phase transition temperature is related to the transition from a tetragonal ferroelectric phase (FE) to a cubic paraelectric phase (PE). The FE to PE phase transition occurs at ≈ 311 and $\approx 139^\circ\text{C}$ for PST25 and PST50, respectively, as seen from Figs. 4(a) and 4(b). For PST25, the dielectric constant at the transition temperature increased with increasing sintering temperature from 1050–1150 $^\circ\text{C}$, and then dropped when the sintering temperature was above 1150 $^\circ\text{C}$ (Table 1). The dielectric constant of PST50 continuously increased with increasing sintering temperatures, and a maximum value was found to be about 7900 from the sample sintered at 1250 $^\circ\text{C}$. The result of the maximum dielectric constant corresponded with the density. It is well known that the dielectric constant is inversely proportional to space charge polarization, and the space charge polarization also depends on the porosity and density of ceramics.^{24,25} Hence, with high density and low porosity, a low space charge and a high dielectric constant are obtained. Furthermore, the dielectric peak of PST25 was broader than PST50, and the dielectric spectrum of PST25 increased rapidly above the phase transition temperature. This was due to the PbO content of PST25 being higher than PST50 and thus, PST25 had a higher loss of PbO which led to the higher space charge polarization.

Sintering temperatures have a strong influence on the crystal structure, microstructure, lattice parameter, tetragonality and dielectric properties of PST ceramics. The lattice anisotropy (c/a) increases with increasing sintered temperatures. With the addition of Sr from 0.25–0.50 mol%, the tetragonality is reduced and the tetragonal to cubic transition of PST sintered ceramics occurred in a systematic manner. The maximum density of PST25 and PST50 ceramic was

discovered in the pellets sintered at 1150 and 1250 $^\circ\text{C}$ respectively, which were related to the dielectric constant. Moreover, the dielectric constant of PST sintered ceramics decreased with the increase in Sr doping content.

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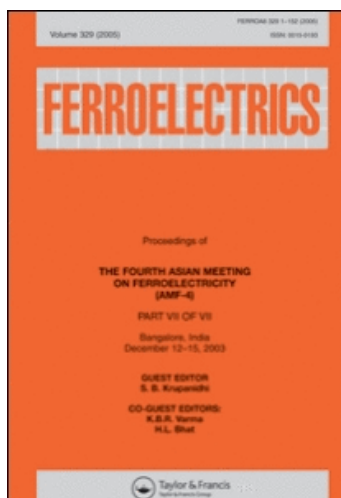
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Effect of Firing Temperatures on Phase and Morphology Evolution of CaZrO_3 Ceramics Synthesized Using the Combustion Technique

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Effect of Firing Temperatures on Phase and Morphology Evolution of CaZrO_3 Ceramics Synthesized Using the Combustion Technique

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The effects of calcination temperatures (900–1400°C) and sintering temperatures (1400–1650°C) on phase and morphology evolution of perovskite CaZrO_3 ceramics were studied. The results obtained from DTA-TGA analysis were used to determine the processed conditions of various calcination temperatures. The highest purity of the orthorhombic perovskite phase was obtained from powder calcined at 1200°C and the pure phase was detected in sintered ceramic samples below 1650°C. The SEM results showed that the average particle size and the average grain size of samples increased with the increase of firing temperatures. The shrinkage of ceramics increased as the sintering temperatures increased. The calcium zirconate, which had around 97.6% of the theoretical density, was obtained from the sample sintered at 1500°C for 2 h. More importantly, the highest density with low sintering temperature were improved by the combustion technique.

Keywords Calcium zirconate; microstructure; combustion technique; density

Introduction

Metal oxides with an ABO_3 perovskite structure are of interest and significance for their electrical properties including: ferroelectricity, piezoelectricity, and superconductivity, and they also offer interesting high temperature properties. Calcium zirconate (CaZrO_3) is a kind of perovskite structure with: high chemical stability, a high melting temperature ($\sim 2345^\circ\text{C}$), good thermal shock resistance, a relatively low thermal expansion coefficient and a phase stability in contrast to zirconia. Therefore, CaZrO_3 has received much attention for mechanical and electrical applications, such as: fuel cells [1], filler [2], coating [3], capacitors [4], resonator for microwave telecommunication [5] and temperature compensating materials of capacitance in multilayer ceramic capacitors.

CaZrO_3 ceramics can be prepared via solid state reaction methods [6, 7]. W. J. Lee *et al.* [6] prepared CaZrO_3 ceramics which obtained a density of around 96% of the theoretical density from a sample sintered at 1650°C for 2 h via the solid state reaction method. To reduce the sintering temperature, the Ni ion was doped in CaZrO_3 ceramics and obtained

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a 95% dense calcium zirconate sample with the sintering temperature higher than 1550°C [7]. It is well known that the conventional solid-state route, which involves prolonged calcination at high temperatures with intermediate grindings, yield large, coarse-grained, micron-sized powders [8, 9]. Presently, the combustion technique is interesting because it can decrease the calcination temperature [10], obtain a pure phase and nanosized particles because of the combustion technique's high surface energy and driving force [11, 12]. So, in this present study, the phase formation and microstructure of CaZrO_3 ceramics were investigated. CaZrO_3 ceramics were prepared using the combustion technique with different calcination and sintering temperatures. The results were also compared with previous works.

Experimental

The starting materials were commercially available: CaCO_3 (99%) and ZrO_2 (99%). Calcium zirconate (CaZrO_3) powder was prepared, using the combustion technique, by thoroughly grinding mixtures of the raw materials by a ball milling procedure (zirconia milling media under ethanol for 24 h). Drying was carried out at 120°C for 4 h. After sieving, the reaction of the uncalcined powders with well-mixed urea taking place during heat treatment was investigated by thermogravimetric and differential thermal analysis (TGA-DTA) using a heating rate of 10°C/min, in air, from room temperature up to 1325°C. The mixture of raw materials and the fuel, urea, was well-mixed before the calcination step. The mixed powders were calcined at temperatures ranging from 900 to 1400°C, with a dwell time of 2 h and a heating/cooling rate of 5°C/min. The calcined powders were then pressed into disks with a diameter of 15 mm at a pressure of 200 MPa. The pellets were sintered at 1400 to 1650°C for 2 h and cooled in a furnace. X-ray diffraction was employed to identify the phase formed and the optimum temperature to prepare the CaZrO_3 powders and ceramics. The calcined powders and sintered ceramics morphologies were imaged using

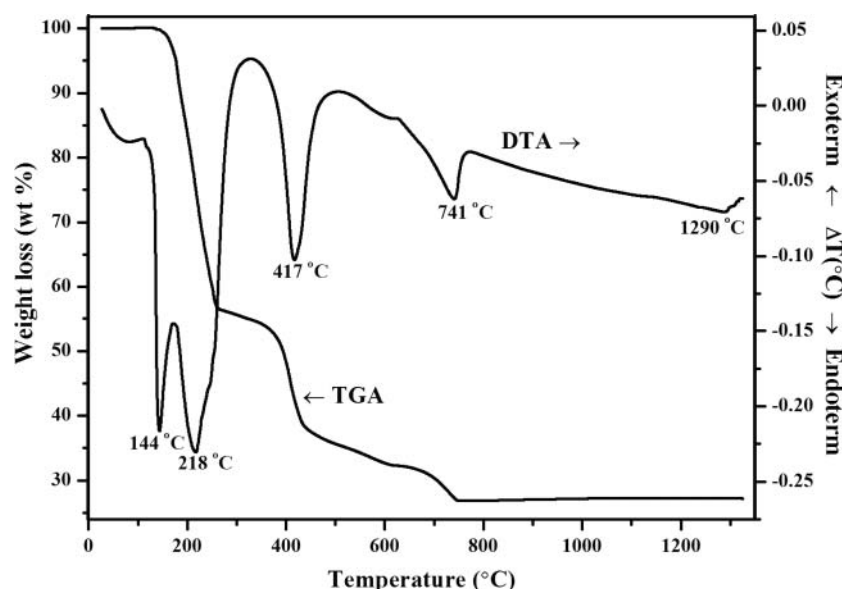


Figure 1. TGA-DTA curves for the mixture of raw materials and urea.

scanning electron microscopy. The density of the sintered ceramics was measured using the Archimedes method. The average particle size and the average grain size were determined by using a mean linear intercept method.

Results and Discussion

The TGA-DTA simultaneous analyses of a powder mixed in the stoichiometric proportions of CaZrO₃ and urea is exhibited in Fig. 1. In the temperature range from room temperature to ~260°C, the sample demonstrates endothermic peaks at 144 and 218°C in the DTA curve, which was consistent with the first weight loss around 102–260°C. These observations can be related to the melting of urea at about 135°C [12]. The second weight loss occurred

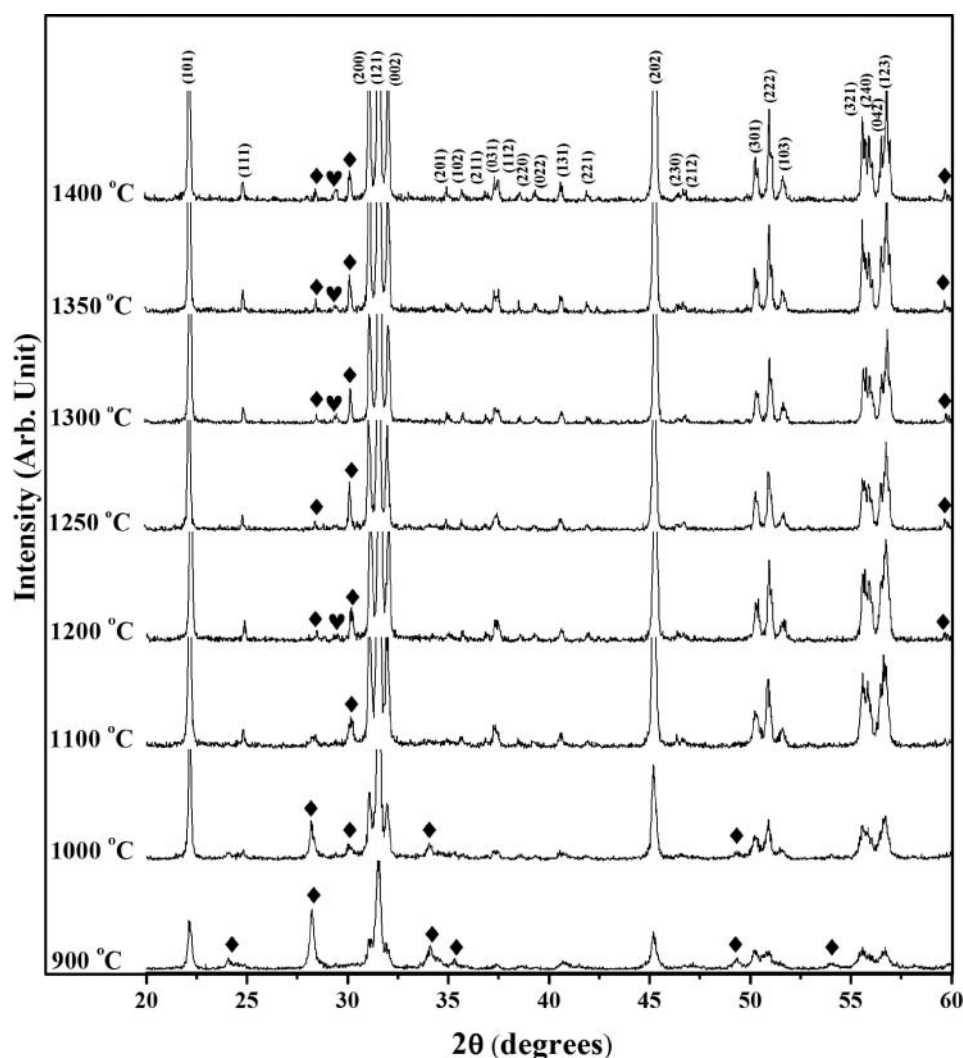
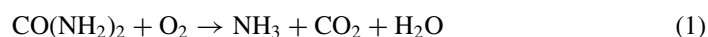


Figure 2. XRD patterns of CaZrO₃ powders calcined at various temperatures for 4 h: (♥) CaCO₃ and (♦) ZrO₂.

between 270 and 420°C, which related to the endothermic peak at 417°C in the DTA curve and was due to the rapid vaporization of water and gas [13], which correlates with following equation:



The third weight loss occurred between 430 and 745°C, which correlated with the small endothermic peaks at 741°C. This probably occurred due to the decomposition of CO_2 in the CaCO_3 [7]. At temperatures higher than 750°C, the last weight loss was nearly stable and the endothermic peak occurred at 1290°C, which might be the solid-state reaction of the raw materials. These results were used to identify the range of different calcination temperatures for XRD investigation.

XRD patterns of the calcined powders are given in Fig. 2. The crystal structure was matched with JCPDS file no. 35-0790 and corresponded to previous works [7, 14]. The diffraction synthesis lines illustrated that the structure of CaZrO_3 , calcined from 900 to 1400°C, indexed a orthorhombic perovskite structure. The crystalline phase of CaZrO_3 was accompanied with ZrO_2 and CaCO_3 as separate phases in all calcination conditions which is similar to previous works [7, 14]. The degrees of the perovskite phase were determined by measuring the major XRD peak intensities of the perovskite phase. The percentage of the perovskite phase was obtained by the following equation:

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{ZrO}_2} + I_{\text{CaCO}_3}} \right) \times 100 \quad (2)$$

This equation is a well-known equation widely employed in connection with the preparation of complex perovskite structure materials [15]. Here I_{perov} , I_{ZrO_2} and I_{CaCO_3} refer to the intensity of the (110) perovskite peak and the intensities in the highest ZrO_2 and CaCO_3 peaks, respectively. The percent of the perovskite phase in CaZrO_3 calcined powders at calcination temperatures ranging from 900 to 1400°C for 2 h is shown in Table 1. The highest percentage of the perovskite phase of CaZrO_3 in the calcined powders-about 97.8% was obtained at the calcination temperature of 1200°C for 2 h.

Figure 3(a), (b) and (c) illustrate the SEM photographs of morphological changes in the calcined CaZrO_3 powders as a function of calcination temperatures. The particles

Table 1
The percent perovskite phase and average particle size of CaZrO_3 powders

Calcined temperature (°C)	Percent perovskite phase (%)	Average particle size (nm)	
		FWHM	SEM
900	84.7	65.9	134.9
1000	91.3	84.5	157.2
1100	97.4	109.9	176.1
1200	97.8	119.9	177.4
1250	96.4	122.1	246.2
1300	96.6	124.5	336.5
1350	97.5	131.9	394.3
1400	97.4	134.6	434.9

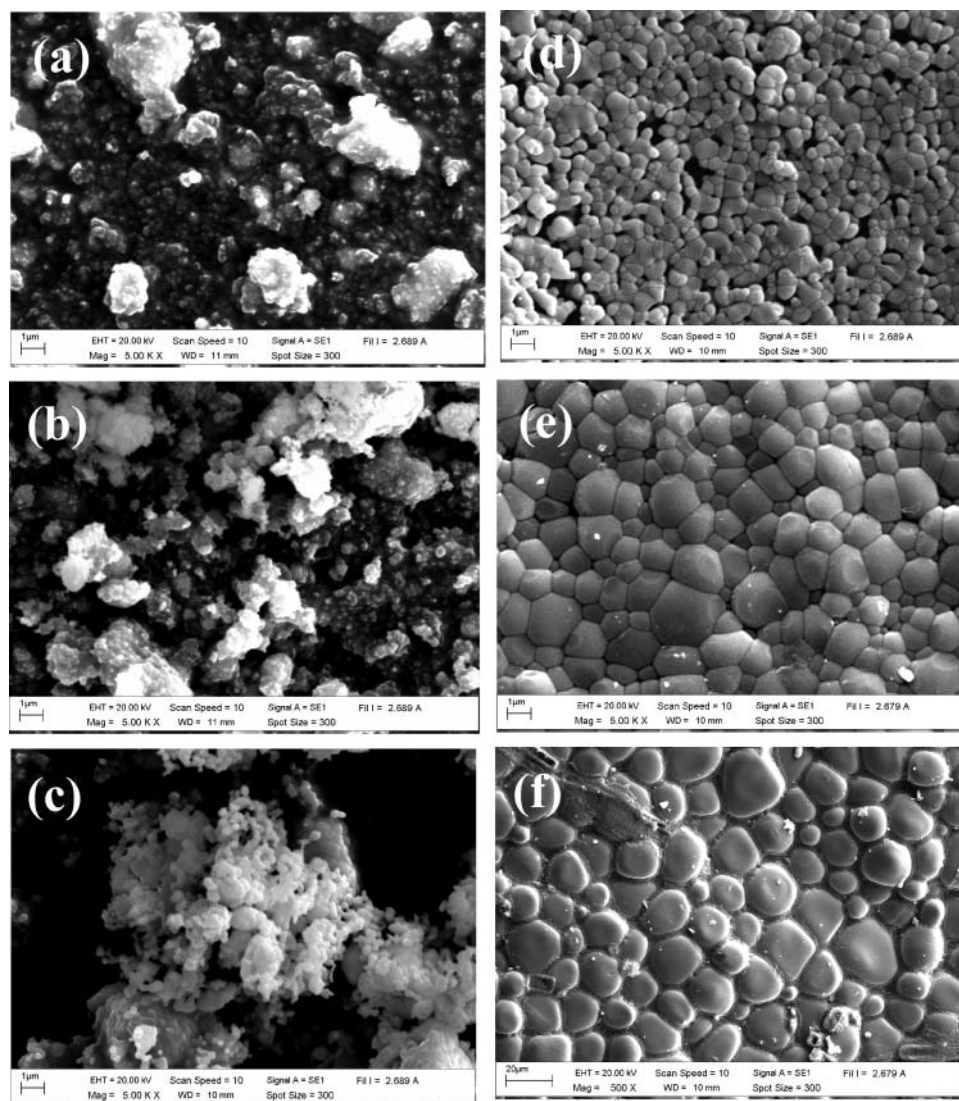


Figure 3. SEM photomicrographs of the powders calcined at : (a) 900°C, (b) 1000°C and (c) 1300°C, for 2 h and the pellets surface sintered at: (d) 1400°C, (e) 1500°C, and (f) 1650°C, for 2 h.

are agglomerated and spherical with a variation in particle size. The average particle size was calculated by the linear intercept method and the Scherrer formula for the major (h k l) reflection of XRD patterns. More agglomerated particles and the increased range of average particle size could be observed as the calcination temperatures increased as shown in Table 1. The average particle size in each condition, measured, from both techniques, had little difference in their values.

The calcined powders obtained at 1200°C were pressed into pellets and sintered from 1400 to 1650°C for 2 h. The phase formation behavior of the sintered ceramics was revealed using the XRD technique as seen in Fig. 4. The CaZrO₃ ceramics were identified as a single phase in sintered samples below 1600°C with a perovskite structure which had

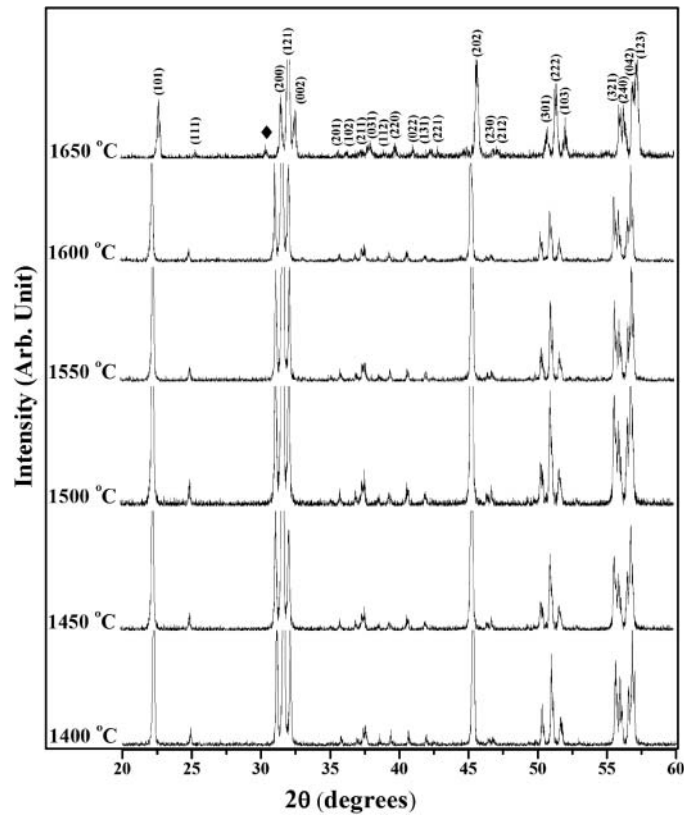


Figure 4. XRD patterns of CaZrO_3 ceramics sintered between 1400 and 1650 °C for 2 h: (◆) ZrO_2 .

an orthorhombic structure. The peak of ZrO_2 was detected at 1650 °C, which may be due to the vaporization of Ca^{2+} at high temperatures. The percent of the perovskite phase of sintered ceramics is listed in Table 2.

The morphological changes in the CaZrO_3 surface of the sintered ceramics as a function of sintered temperatures are displayed in Fig. 3(d), (e) and (f). It was evident that the porosity

Table 2

The percent perovskite phase, shrinkage, density and average grain size of CaZrO_3 ceramics

Sintered temperature (°C)	Percent perovskite phase (%)	Shrinkage (%)	Density		Average grain size (μm)
			(g / cm^3)	Theoretical (%)	
1400	100	12.55	4.27	92.6	0.55
1450	100	14.45	4.33	93.9	0.92
1500	100	15.28	4.50	97.6	1.26
1550	100	15.11	4.42	95.9	5.20
1600	100	8.50	4.41	95.7	9.40
1650	93.7	6.33	3.85	83.5	16.84

decreased, but the average grain sizes increased from 0.55 to 16.84 μm when the sintering temperatures increased from 1400 to 1650°C, as shown in Table 2. When the sintered temperature was higher than 1500°C, the melting of grain boundary began and continually increased as the sintered temperature increased as shown in Fig. 3(f).

The density and the percent of shrinkage of CaZrO₃ ceramics as a function of the different sintering temperatures are illustrated in Table 2. The density and the percent of shrinkage in value was first increased by sintering temperatures and reached its highest at 1500°C and reduced in value at higher sintering temperatures. The maximum density was around 4.50 g/cm³ or ~97.6% of the theoretical density of the sintered sample at 1500°C for 2 h. During the sintering process, the densification mechanisms during treatment corresponded to the XRD results and the grain growth, especially at the final stage of sintering. That the density decreases when the sintering temperature is higher than the optimal temperature may be due to distending from the trapped gas in the pores. The gas-filled pores combined and grew owing to the grain growth [16]. The lower sintering temperature and higher density were obtained from the combustion technique, compared to the solid-state reaction method [6, 7]. This demonstrated the efficiency of the combustion technique in the preparation of pure and dense CaZrO₃ ceramics.

Conclusions

The maximum percentage (97.8%) of the pure orthorhombic perovskite phase was obtained with a calcination temperature of 1200°C. The maximum density of the pure pellet was ~97.6% of the theoretical density from the sintered ceramic at 1500°C for 2 h. The range of the average particle size and average grain size increased with the increase of calcination and sintering temperatures. The melting and combustion of urea carry out an important role in the complete process. The calcination and sintering temperatures have a strong influence on the crystal structure, homogeneity, microstructure and density of the calcined powders and the sintered ceramics.

Acknowledgments

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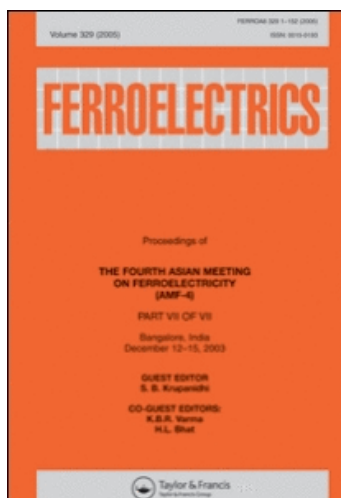
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Use of the Combustion Technique for the Preparation of $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$ Ceramics

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Use of the Combustion Technique for the Preparation of $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$ Ceramics

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The preparation conditions for barium titanate zirconate $[\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3]$ ceramics by the combustion method were studied. The X-ray diffraction pattern indicated that the calcined powders belonged to a cubic phase. The maximum percentage of the cubic perovskite phase was found in the sample calcined at 850°C. A pure cubic crystal structure was found in all ceramic samples. The average grain size increased with increasing sintering temperatures. The dielectric constant-temperature plots showed a maximum peak value of 5800 from ceramic sintered at 1350°C. The densities of samples corresponded to the dielectric constant. A diffuse phase transition was also observed.

Keywords Barium titanate zirconate; microstructure; phase formation; dielectric constant; combustion technique

Introduction

Barium titanate (BaTiO_3) is one of the most widely used materials in the electronic industry. Because of its specific characteristics, such as a high dielectric constant, low dielectric loss and good piezoelectricity, it's used for a variety of applications such as: multilayer ceramic capacitors (MLCCs), resistors, thermal sensors, etc. [1, 2]. The structural phase of BaTiO_3 changes from tetragonal to cubic at a Curie temperature (T_c) which occurs around 120–130°C. For the perovskite ABO_3 , substituting the A and/or B cation site by isovalent ions-, such as the addition of lead (Pb) into the barium (Ba) site or zirconium (Zr) into the titanium (Ti) site in barium titanate-, it can improve the electrical properties of the materials [3].

Zr-substitution at the Ti-site in BaTiO_3 decreases the temperature and broadens the permittivity maximum [4]. The zirconium ion content increases, the orthorhombic-tetragonal phase transition temperature increases and the tetragonal-cubic phase transition temperature decreases [5, 6]. For $x \geq 0.15$, the three phase transitions merged together. In addition, the transition temperature of barium titanate zirconate ($\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$) shifts to a lower

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temperature region, while the degree of diffuse phase transition behavior is enhanced with the increase of Zr content. For the $x > 0.25$, the sample showed broad dielectric peaks with frequency distortion, i.e., ferroelectric-relaxor behavior [7]. The dielectric study of the $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$ ceramics showed a tenability of 26% and a high value of figure of merit (FOM) of 104. These make $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$ ceramics suitable for dynamic random access memories, tunable microwave devices and capacitors.

The solid state reaction method is widely used in the preparation of barium titanate zirconate ceramics [8–10]. Nevertheless, the solid state reaction method requires high temperatures to prepare the ceramics and large particle sizes and wide particle size distribution obtained. The combustion route has interesting characteristics such as: its simplicity, its relatively low cost and a nanosize with a high surface energy and driving force. The combustion route also reduces the firing temperatures which would save energy [11]. However, no researcher has reported the preparation of $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$ by the combustion route and no one has shown the results of firing conditions on phase formation and the microstructure of $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$. Thus, in this research, $\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$; BTZ was fabricated by the combustion route. The effects of the firing temperatures on the crystal structure, morphology and dielectric properties of the samples were examined and the results are discussed.

Experimental Procedure

The starting materials were commercially available barium carbonate, BaCO_3 (99%) titanium (IV) oxide, TiO_2 (99%) and zirconium (IV) oxide, ZrO_2 (99%). Barium titanate zirconate ($\text{Ba}(\text{Ti}_{0.70}\text{Zr}_{0.30})\text{O}_3$, BTZ) powder was synthesized by the combustion of thoroughly ground mixtures of raw materials by a ball milling procedure (zirconia milling media under ethanol for 24 h). Drying was carried out at 120°C for 4 h. After sieving, the powders and urea were mixed in an agate mortar. Then, the mixture was calcined at various calcination temperatures, ranging from 600 to 900°C , with a dwell time of 4 h. and heating/cooling rate of $5^\circ\text{C}/\text{min}$. The calcined powders were then pressed into disks with a diameter of 15 mm at a pressure of 40 MPa. The pellets were sintered from 1300 to 1450°C for 2 h. and cooled in a furnace. For electrical measurements, silver paste was fired on both sides of the polished samples at 500°C for 30 min and used as electrodes.

X-ray diffraction was employed to identify the phase formed and optimum temperature of BTZ powders and ceramics. Calcined powders and sintered ceramics morphologies were imaged using scanning electron microscopy (SEM). The average particle size was computed from Full Width at Half Maximum (FWHM) using the Scherrer formula. Densities of the sintered ceramics were measured by the Archimedes method and the average grain size was determined by using a mean linear intercept method. The capacitance was measured with a LCR meter. The dielectric constant (ϵ_r) was calculated using the geometric area and thickness of the discs.

Results and Discussion

XRD patterns of BTZ powders calcined at various temperatures are plotted in Fig. 1. The structure of the BTZ powders belonged to the cubic perovskite phase and could be matched with JCPDS file number 36–0019 [12]. However, the raw materials such as BaCO_3 , ZrO_2 and BaTiO_3 appeared in all BTZ samples. The percentage of the perovskite phase of BTZ powders at various calcination temperatures was computed and is listed in Table 1. The percentage of the BTZ perovskite phase increased with the increase of calcination

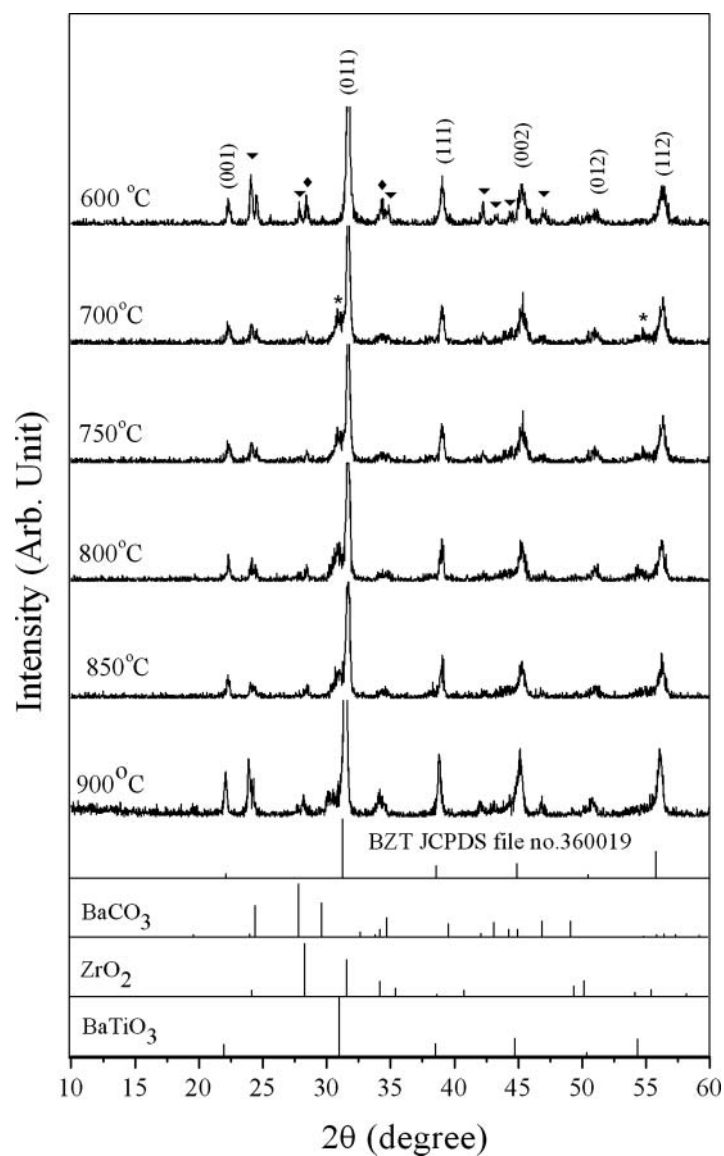


Figure 1. XRD patterns of BTZ powders at various calcination temperatures; (▼) BaCO_3 , (◆) ZrO_2 , (*) BaTiO_3 .

temperatures up to 850°C , and then it decreased with higher calcination temperatures. The maximum percent perovskite phase (98%) was found in the powder calcined at 850°C . The average particle size calculated from Full Width at Half Maximum (FWHM) using the Scherrer formula for the major (h k l) reflection of the XRD peaks is shown in Table 1 [13]. The nano-particle size tended to increase as calcination temperatures increased.

SEM photographs of BTZ powders calcined at different temperatures are shown in Fig. 2(a) and (b). It is clearly seen that the powders have a spongy appearance, forming

Table 1

The % perovskite phase, average particle size, average grain size, density and maximum dielectric constant of BTZ samples

Calcined powders			Sintered ceramics			
Calcination temperatures (°C)	% perovskite phase	Average particle size (μm)	Sintering temperatures (°C)	Average grain size (μm)	Density (g/cm ³)	Maximum dielectric constant
600	90	89	1300	2.8	5.53	3800
700	92	109	1350	21.2	5.67	5800
750	95	116	1400	38.3	5.44	5400
800	96	125	1450	43.1	5.42	4600
850	98	133				
900	95	156				

agglomerates of fine particles of different shapes. As the temperature increased, more agglomerate particles could be observed.

The powder calcined at 850°C was pressed into a pellet and sintered between 1300 and 1450°C for 2 h. XRD patterns of BTZ ceramics sintered at various temperatures are plotted in Fig. 3. All samples were free from minor phase. BTZ ceramics are identified as a

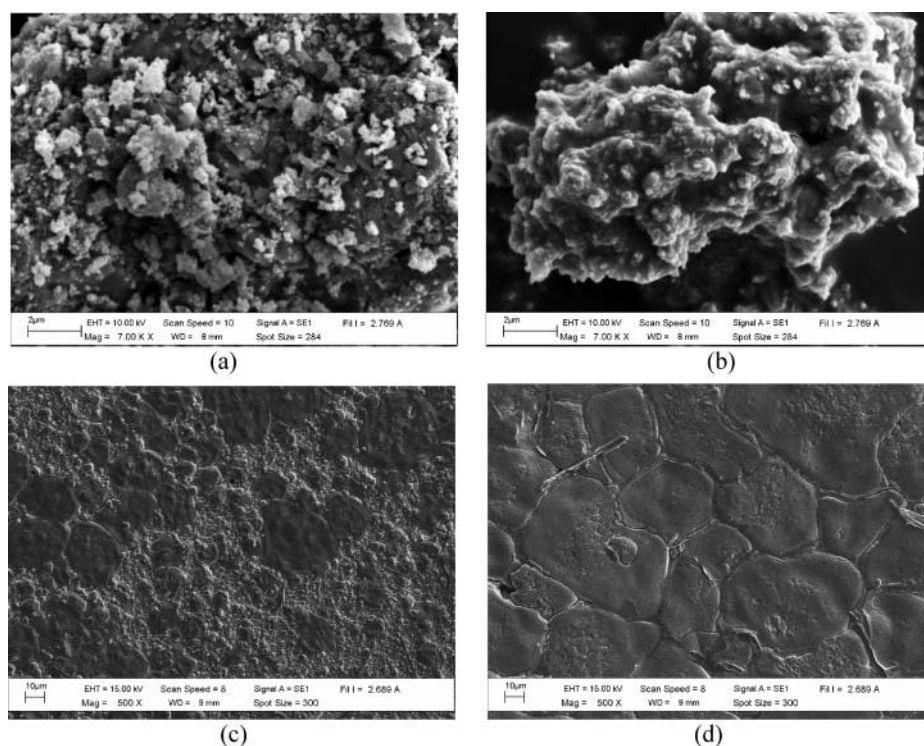


Figure 2. SEM morphology of BTZ samples: (a) powder calcined at 700°C, (b) powder calcined at 900°C, (c) ceramic sintered at 1300°C and (d) ceramic sintered at 1450°C.

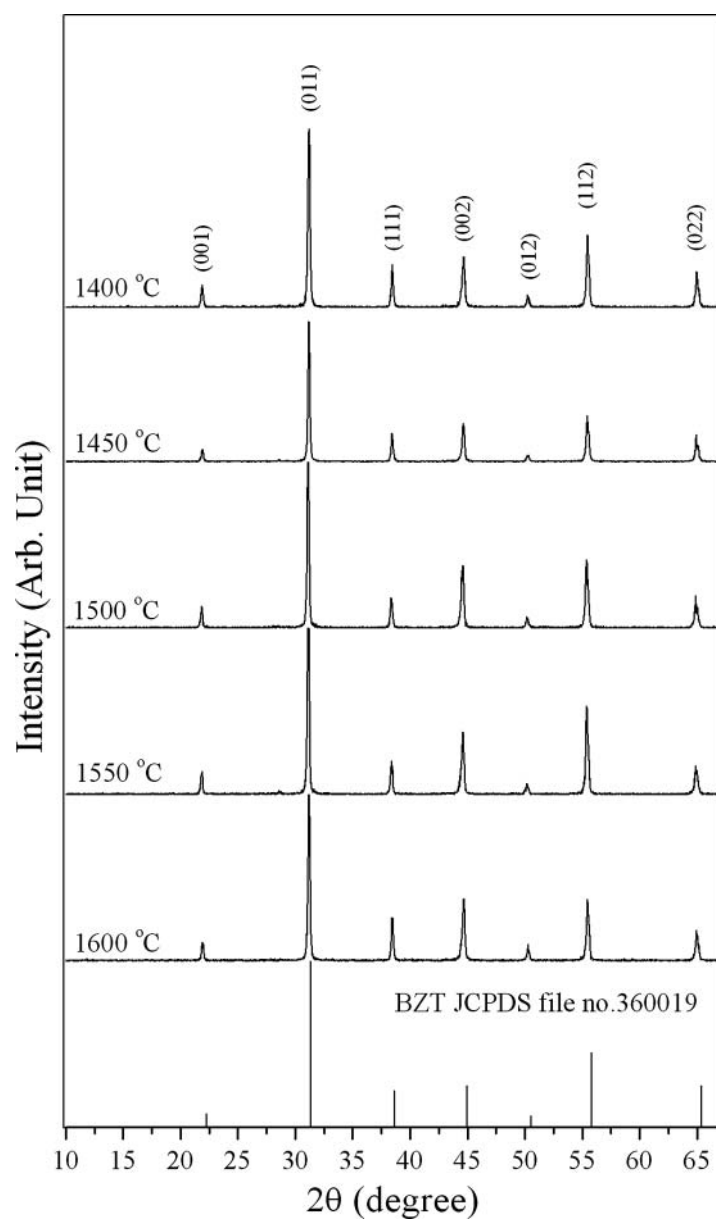


Figure 3. XRD patterns of BTZ pellets with various sintering temperatures.

single phase with a perovskite structure which has a cubic symmetry, the same as reported in previous investigations [14]. Although the second phase was found in the calcination procedure, they disappeared in the sintering step. There was evidence that the combustion route could produce the pure cubic phase of BTZ ceramics.

Microstructure developments of sintered pellets were investigated by SEM. The surface of BTZ ceramics at various sintering temperatures are shown in Fig. 2(c) and (d). The results showed a nonuniform distribution of grain size at low sintering temperatures. The

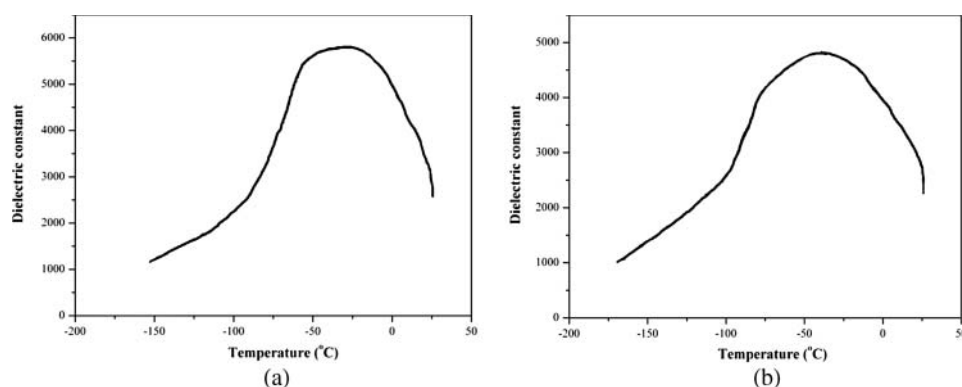


Figure 4. The dielectric constant of BTZ ceramics: (a) 1350°C and (b) 1450°C.

average grain sizes increased from 2.8 to 43.1 μm (Table 1) with the increase of sintering temperature from 1300° to 1450°C. These results agreed with previous work [15]. The rapid increase in grain size may be due to the atom in vicinity of particular grain boundary which will have a driving force to diffuse towards that boundary and will diffuse when the temperature is sufficiently elevated [16].

The density of sintered pellets measured by the Archimedes method is listed in Table 1. As the sintering temperature increased, the density of samples increased up to 5.67 g/cm³ or 96.1% of theoretical density in samples sintered at 1350°C, and then decreased with higher sintering temperatures. The temperature dependence of the dielectric constant at 1 kHz for BTZ ceramics sintered at 1350 and 1450°C is shown in Fig. 4. The Curie temperature (T_c) slightly decreased from -28 to -43°C , while the BTZ30 prepared with mixed oxide showed the T_c at approximately -64°C . The T_c of the samples prepared by the combustion technique was higher than the samples prepared by the solid state reaction method; this was similar to previous work [17]. The maximum dielectric constant was discovered in samples sintered at 1350°C. It was noticed that the dielectric constant corresponded with the density of sintered pellets.

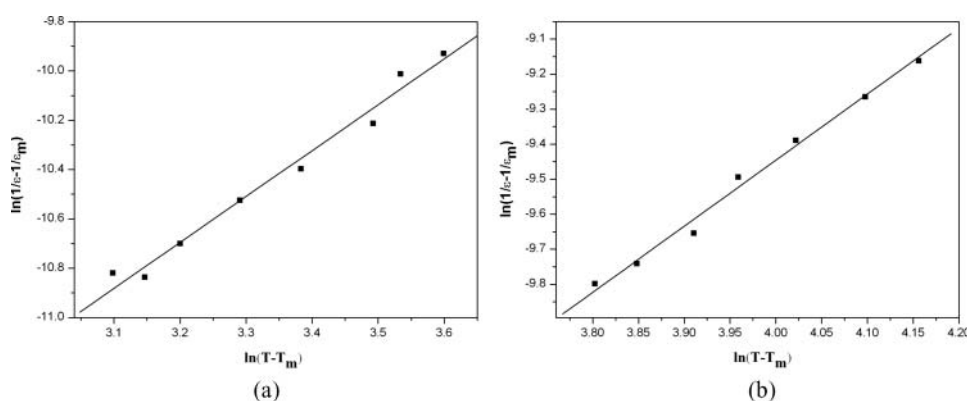


Figure 5. Plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ for BTZ30 ceramics at sintering temperature: (a) 1350°C and (b) 1450°C.

The diffuse phase transition around the transition temperature can be obtained from the broadening in the dielectric constant versus temperature curve which is characterized by a modified Curie-Weiss law [18].

$$1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C' \quad (1)$$

Where C' is the Curie-Weiss constant. The parameter γ describes the character of the phase transition; for $\gamma = 1$ a normal Curie-Weiss law is obtained; $\gamma = 2$ describes a complete diffuse phase transition [15].

Figure 5 shows the plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ for the BTZ30. The γ value was computed from the slope of the fitting curves using the equation 1. The γ value was found to be about 1.92–1.94 which was close to the $\gamma (= 1.87)$ of previous work [19]. This indicated that the BTZ30 has a strong diffuse phase transition and a relaxor-type diffuse phase permittivity.

Conclusions

The calcination and sintering temperatures affected the phase formation, microstructure, particle size, grain size, density, and dielectric properties. The resulting BTZ powders had a spongy appearance and become more agglomerated as the calcination temperature increased. BTZ ceramic was identified by XRD as a phase with a perovskite structure having cubic symmetry. The densest of 96% of theoretical density and a maximum dielectric constant of 5800 were obtained from the sample sintered at 1350°C. These confirmed that the combustion technique can prepare good BTZ30 ceramics. The γ value also exhibited the ferroelectric-relaxor behavior of BTZ30.

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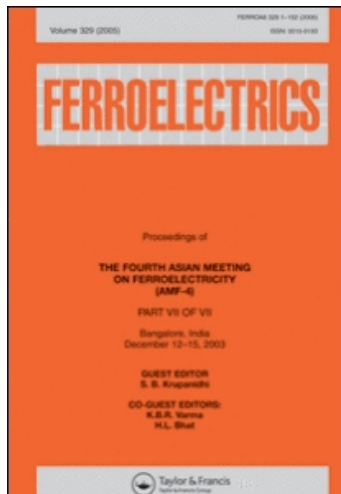
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Crystal Structure and Microstructure of $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ Ceramics Prepared by the Solid State Reaction Method

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Lead Barium Zirconate Titanate $[(\text{Pb}_{1-x}\text{Ba}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3]$: PBZT ceramics with $x = 0.05$ and 0.10 and $0 \leq y \leq 1$ were prepared by the solid state reaction method. The calcination temperatures were between 800 and 1000°C for 1 h and the sintering temperature was 1300°C for 3 h. The crystal structure and microstructure were characterized by a X-ray diffractometer (XRD) and scanning electron microscopy (SEM). It was found that the structure of calcined powders and sintered pellets of $x = 0.05$ and 0.10 were in an orthorhombic phase for $y = 0$, and tetragonal phase for $0.5 \leq y \leq 1$; the c/a ratio increase with an increasing in the y content, whereas the orthorhombic and tetragonal phase coexist for $y = 0.25$. Microstructurally, the average particle size and average grain size slightly decreased with an increasing in the y content. The density and shrinkage increased when the x content increased.

Keywords Lead barium zirconate titanate; microstructure; phase formation; crystal structure

Introduction

Lead barium zirconate $(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$; PBZ is one of the perovskite structure materials which was discovered by Roberts in 1950 [1, 2]. The investigation of the structural phase indicated that the PBZ has an anti-ferroelectric phase and orthorhombic structure at room temperature. The anti-ferroelectric to ferroelectric phase transition of PBZ produces a large increase in volume [3, 4]. Specifically, the PBZ with $x = 0.10$ exhibited high expansion (0.85%) which makes this ceramic interesting for potential use in large displacement actuator devices [5–7].

Lead barium titanate $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$; PBT is perovskite ferroelectric material which has a tetragonal structure at room temperature [8–10]. It changes from ferroelectric to paraelectric when it receives the proper temperature, i.e. Curie temperature. Moreover, PBT with $x = 0.10$ shows a high Curie temperature ($\sim 450^\circ\text{C}$), and has been used to manufacture many electric and optical devices [10].

Lead barium zirconate titanate; PBZT ceramics is a solid system composed of anti-ferroelectric PBZ and ferroelectric PBT. The structural phase and properties of PBZ differ

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absolutely from PBT. This suggests that the amounts of Zr^{4+} and Ti^{4+} ions on the B-site were directly affected by the phase formation, microstructure and physical properties of PBZT. However, the crystal structure and microstructure of lead barium zirconate titanate $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$: $x = 0.05$; PBZT5 and 0.10; PBZT10 ceramics with $0 \leq y$

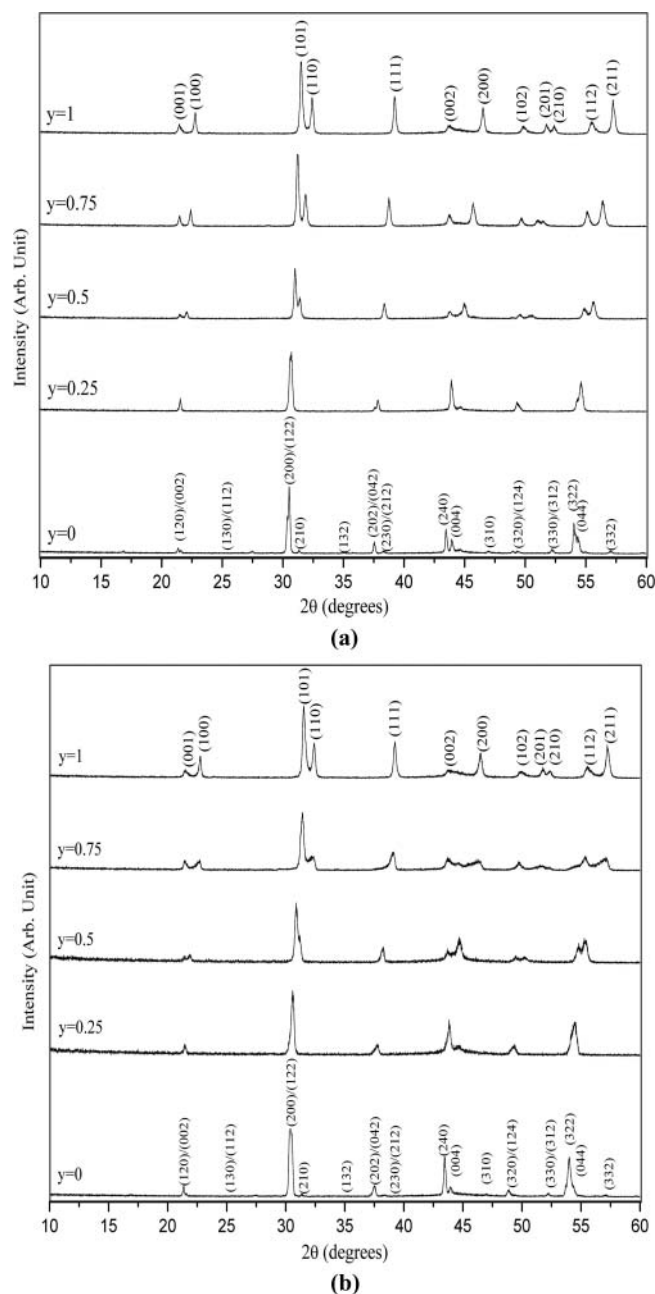


Figure 1. XRD pattern of PBZT powders with (a) PBZT5 and (b) PBZT10.

≤ 1 ceramics prepared by the solid state reaction method has rarely been reported in the literature. So, PBZT5 and PBZT10 ceramics with $0 \leq y \leq 1$ were prepared by the solid state reaction method. The structural phase and microstructure of PBZT ceramics were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM).

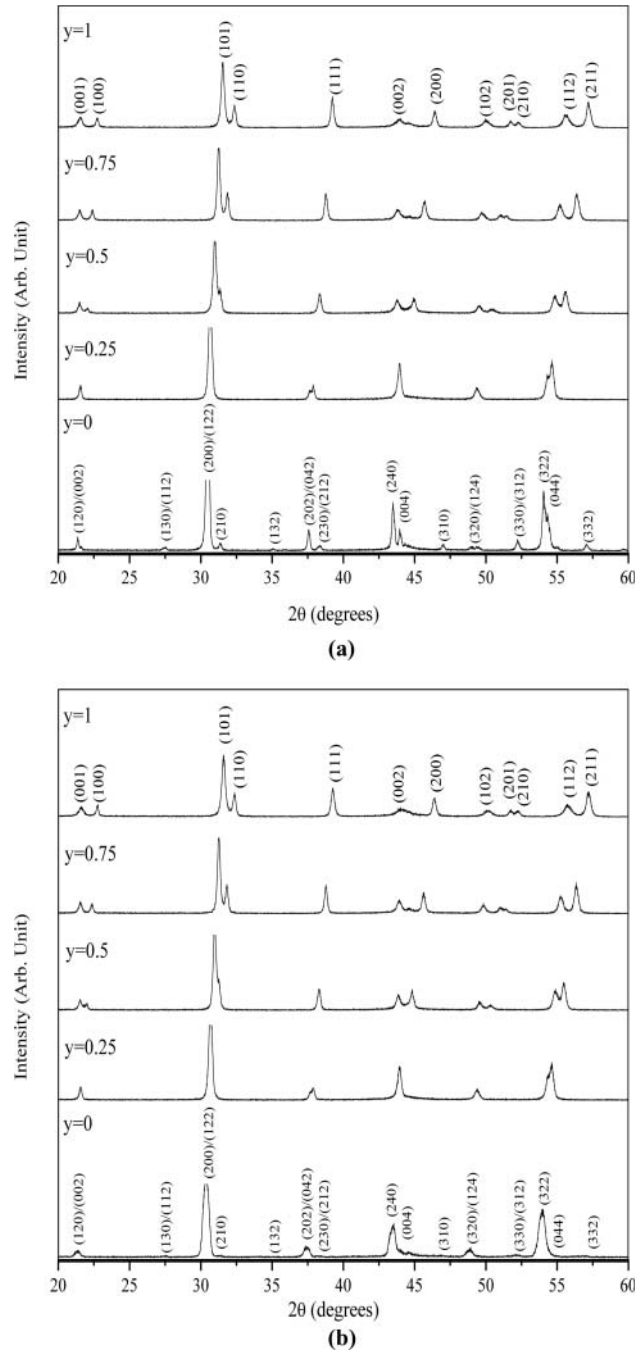


Figure 2. XRD pattern of PBZT ceramics with (a) PBZT5 and (b) PBZT10.

Table 1
The crystal structure, lattice parameter a , b and c , c/a ratio, unit cell volume and average particle size of PBZT powders

x	y	Crystal Structure	Lattice Parameter (Å)			c/a ratio	Unit cell volume (Å ³)	Average Particle Size (μm)
			a	b	c			
0.05	0	orthorhombic	5.8890	12.1982	8.3748	—	601.6054	1.413
	0.25	tetragonal+ orthorhombic	—	—	—	—	—	1.375
	0.50	tetragonal	4.0302	4.0302	4.1481	1.0293	67.3756	1.305
	0.75	tetragonal	3.9714	3.9714	4.1468	1.0442	65.4034	1.694
	1	tetragonal	3.9037	3.9037	4.1414	1.0609	63.1103	0.691
0.10	0	orthorhombic	5.8986	12.1954	8.4080	—	604.8361	1.268
	0.25	tetragonal+ orthorhombic	—	—	—	—	—	1.108
	0.50	tetragonal	4.1224	4.1224	4.1798	1.0139	71.0323	1.407
	0.75	tetragonal	4.0592	4.0592	4.1433	1.0207	68.2696	1.653
	1	tetragonal	3.9074	3.9074	4.1420	1.0600	63.2391	0.674

Table 2
The lattice parameter a , b and c , c/a ratio, unit cell volume, average grain size, density and shrinkage of PBZT ceramics

Compositions		Lattice parameter (Å)			c/a ratio	Unit cell volume (Å ³)	Average grain size (μm)	Density (g/cm ³)	Shrinkage (%)
x	y	a	b	c					
0.05	0	5.3422	11.4772	7.8583	—	481.8199	2.08	7.45	13.24
	0.25	—	—	—	—	—	2.11	7.46	16.22
	0.50	4.0357	4.0357	4.1382	1.0254	69.1102	2.24	7.47	17.24
	0.75	3.9678	3.9678	4.1364	1.0425	67.8883	2.36	7.49	17.48
0.10	1	3.9137	3.9137	4.1158	1.0516	66.2973	1.69	7.54	18.34
	0	5.3634	11.469	7.8802	—	484.7334	1.90	7.39	14.74
	0.25	—	—	—	—	—	2.17	7.43	16.27
	0.50	4.0509	4.0509	4.1339	1.0205	67.8364	2.15	7.45	16.96
	0.75	3.9761	3.9761	4.1273	1.0380	65.2500	2.21	7.47	17.03
	1	3.9152	3.9152	4.1115	1.0501	63.0243	1.97	7.50	17.45

Experimental

The $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$: $x = 0.05$; PBZT5 and 0.10; PBZT10 ceramics with $0 \leq y \leq 1$ were prepared by a conventional solid state reaction method. The raw materials of PbO , BaCO_3 , ZrO_2 and TiO_2 were weight and mixed by ball milling in ethanol using zirconia balls for 24 h. After drying and sieving, it was calcined between 800 and 1000°C for 1 h [11]. The calcined powders were reground by ball-milling and mixed with 2 wt% binder for 24 h. The calcined powders were then dried, crushed and sieved. Pellets of 15 mm in diameter were isostatically pressed at 80 MPa. Finally, the pellets were sintered at 1200°C for 3 h. In order to minimize the loss of lead due to vaporization, the PbO atmosphere during the sintering process was maintained using lead titanate and lead zirconate as the spacer powders. The crystal structure and microstructure of the calcined and sintered samples were characterized by a X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The Archimedes displacement method with distilled water was employed to evaluate the sample density.

Results and Discussion

Figure 1(a) and (b) shows the XRD pattern of PBZT5 and PBZT10 powders with $0 \leq y \leq 1$. The pure perovskite phase of both PBZT5 and PBZT10 were observed for all

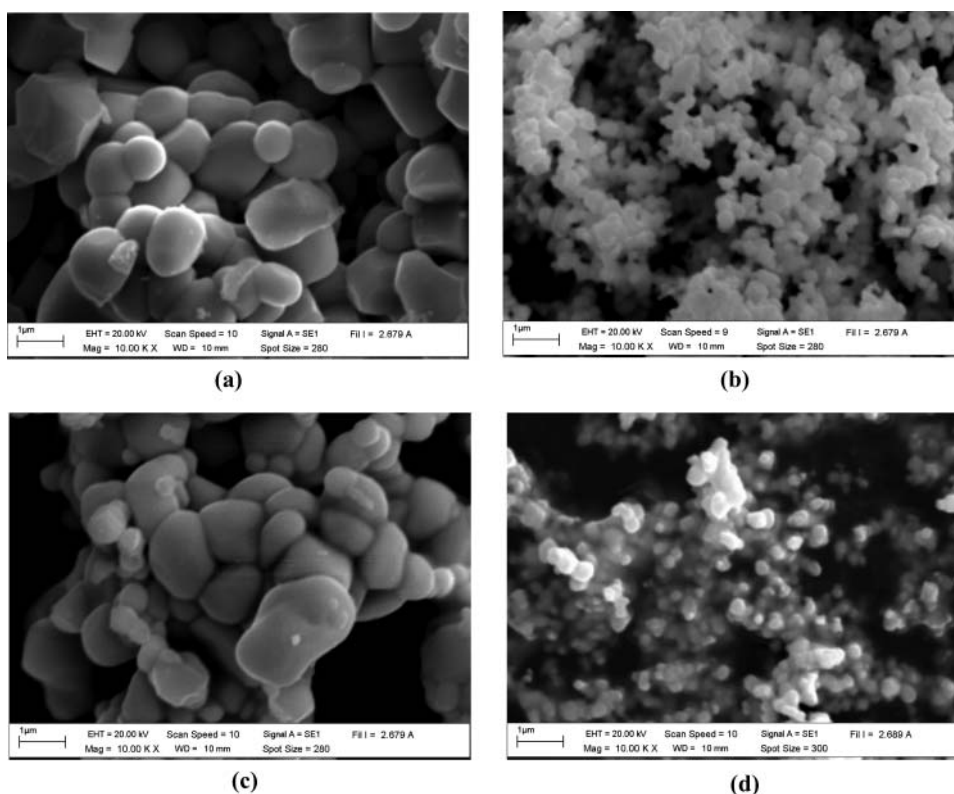


Figure 3. SEM morphology of PBZT5 powders with (a) $y = 0$, (b) $y = 1$ and PBZT10 powders with (c) $y = 0$ and (d) $y = 1$.

compositions. The structural phase of PBZT5 and PBZT10 powders with $y = 0$, indexed in an orthorhombic phase which matched with JCPDS file number 35-0739 [12]. PBZT5 and PBZT10 powders with $0.5 \leq y \leq 1$, indexed in a tetragonal phase which matched with JCPDS file number 06-0452 [13]. The PBZT5 and PBZT10 powders with $y = 0.25$, indexed as the mixed phase between the orthorhombic and the tetragonal phase. The XRD pattern of the orthorhombic phase is known to contain a large number of superlattice reflection, i.e. 130/112, 210, 132, 230/212, 310, 320/124, 330/312 and 332 reflections [5–7]. These superlattice reflections vanished in the XRD patterns of PBZT5 and PBZT10 with $y = 0.25$. It is well known that the XRD pattern of the tetragonal phase obtains the doublet reflections of 001,100 and 002,200 which are indexed as 120,002 and 240,004 in orthorhombic phase. These reflections appeared as a singlet peak in the XRD pattern of PBZT5 and PBZT10 with $y = 0.25$ content. These observations confirmed that the orthorhombic and tetragonal coexist in PBZT5 and PBZT10 samples with $y = 0.25$. The XRD results of PBZT5 and PBZT10 sintered pellets showed similarity with the XRD powders results as shown in Fig. 2(a) and (b). The reflection peaks of PBZT5 and PBZT10 ceramics were sharper than the powders in every y value, which indicates the larger crystallization was obtained from the sintered processing. The lattice parameters a , b , c , of PBZT5 and PBZT10 powders and ceramics were calculated and are shown in Table 1 and 2. In PBZT5 and PBZT10 powders and ceramics with $0.5 \leq y \leq 1$, the lattice parameters a and c decreased with increased y values. The c/a ratio of both PBZT5 and PBZT10 powders and ceramics increased while

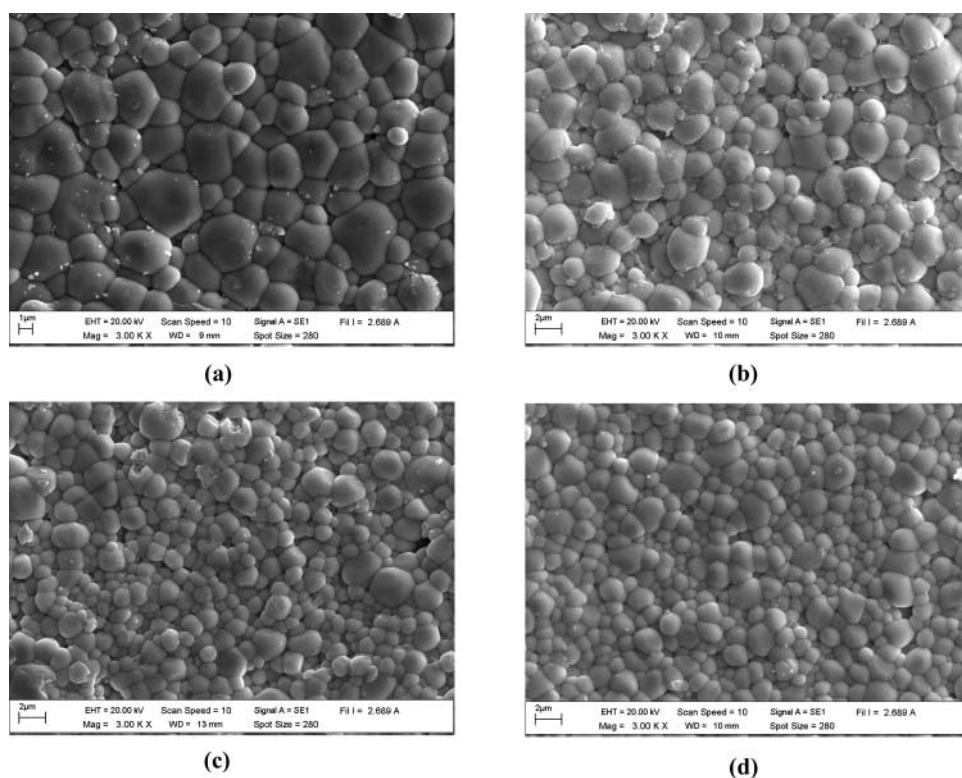


Figure 4. SEM morphology of PBZT5 ceramics with (a) $y = 0.25$, (b) $y = 1$ and PBZT10 ceramics with (c) $y = 0.25$ and (d) $y = 1$.

the unit cell volume decreased when values of y increased as seen in Table 1 and 2. In each composition, the c/a value of the ceramics is higher than the powders.

The SEM morphology of PBZT5 and PBZT10 powders with $y = 0$ and 1 are shown in Fig. 3(a), (b), (c) and (d). The particles of PBZT5 and PBZT10 were agglomerate and irregular in shape with variation in particle size. The average particle size of PBZT5 and PBZT10 of $0 \leq y \leq 0.75$ had little difference in their values, while the value in size of $y = 1$ rapidly decreased. The average particle size was between 0.69 and $1.69 \mu\text{m}$ for PBZT5 and 0.67 and $1.65 \mu\text{m}$ for PBZT10 with an increase of y values as shown in Table 1. The morphological changes in the PBZT5 and PBZT10 surface as a function of the increasing of y are shown in Fig. 4(a), (b), (c) and (d). The increase of the average grain sizes were between 1.69 and $2.36 \mu\text{m}$ for of PBZT5 and between 1.90 and $2.21 \mu\text{m}$ for PBZT10 when the content of y increased from 0 to 1 as illustrate in Table 2.

The measured density and shrinkage with the variation of the y contents are shown in Table 2. The density and shrinkage tended to increase with the increase in y values. The maximum density was obtained around 7.54 g/cm^3 from the PBZT5 sample with $y = 1$ and 7.50 g/cm^3 from the PBZT10 sample with $y = 1$. This indicated that the increase of y value in the PBZT5 and PBZT10 composition affected the density and shrinkage.

Conclusions

The structural phase of $(\text{Pb}_{1-x}\text{Ba}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$: $x = 0.05$; PBZT5 and 0.10; PBZT10 samples were in an orthorhombic phase for $y = 0$ and a tetragonal phase for $0.5 \leq y \leq 1$. The samples were in a mixed phase between orthorhombic and tetragonal phase for $y = 0.25$. The average particle was 0.67 – $1.69 \mu\text{m}$ and the average grain size was 1.69 – $2.36 \mu\text{m}$. The density and shrinkage of PBZT5 and PBZT10 tended to increase with an increase in the x contents. It's indicated that the Zr^{4+} and Ti^{4+} ions have strong influence on the structural phase and microstructure of PBZT.

Acknowledgments

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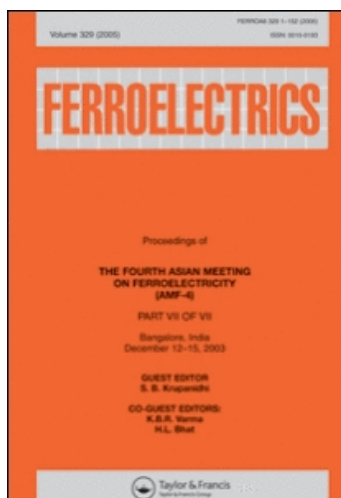
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Fabrication of $(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$ Ceramics via the Combustion Technique

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Fabrication of $(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$ Ceramics via the Combustion Technique

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$(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$ with $x = 0, 0.1$ and 0.2 (PZ, PBZ10 and PBZ20) ceramics were synthesized via the combustion technique. $(\text{CO}(\text{NH}_2)_2)$ was used as fuel to reduce the reaction temperature. The sintering temperatures were in the range of 1150°C – 1350°C for 3 h. All calcined powders indexed in an orthorhombic structure and the purity of the perovskite phase was found in all the sintered pellet samples. The sintered pellets indexed in the orthorhombic structure for PZ and PBZ10 ceramics and in the rhombohedral structure for PBZ20 ceramics. The average grain size increased with an increase of sintering temperatures. The maximum density was observed in the sample sintered at 1250°C . The DSC measurement showed FE-PE phase transition temperature to be around 232°C , 194°C and 154°C , and the PE-FE phase transition temperature was around 229°C , 192°C and 152°C for $x = 0, 0.1$ and 0.2 , respectively. The AFE to FE phase transition temperature was 229°C for PZ ceramics. The dielectric properties were also investigated.

Keywords Lead barium zirconate; combustion technique; sintering temperatures; antiferroelectric

Introduction

Lead zirconate, PbZrO_3 , is a well known antiferroelectric material which has an orthorhombic structure at room temperature. The transition to the cubic paraelectric (PE) phase occurs at around 235°C but a transition from the orthorhombic antiferroelectric (AFE) structure to a rhombohedral ferroelectric (FE) structure occurs a few degrees below the paraelectric transition temperature [1, 2]. The AFE $\rightarrow$ FE phase transition is accompanied by a large volume expansion, which makes this material potentially useful for actuator application. The temperature range over which the FE phase is stable can be extended by chemical substitution, such as Ba^{2+} on the Pb^{2+} sites to form $(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$ (PBZ) solid solutions [3–11]. The substitution of Ba^{2+} for Pb^{2+} in PbZrO_3 is of considerable interest for transducer applications since its volume change, associated with a field force from AFE to FE transition, increases with the Ba^{2+} substitution [10].

PBZ powders were prepared via the solid state reaction method with calcination temperatures about 1000°C for 1 h [7, 12–14]. In general, the vapor pressure of PbO is quite high, above 800°C [10]. This caused a PbO loss during the calcined step and the composition

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and properties of PBZ were changed. To reduce the calcined temperature, Pockarel *et al.* synthesized PZ and PBZ via a semi-wet route [8–14]. The PbO and BaCO₃ were reacted by a co-precipitation technique. The (Pb_{1-x}Ba_x)CO₃ and ZrO₂ were calcined by the solid state reaction method at 700°C for 6 h and subsequently at 850°C for 6 h. However, the calcination temperature of the semi-wet method had higher temperature than the PbO vaporization temperature. Recently, PBZ powders synthesized via the combustion technique has been reported [15]. Nano-size PBZ powders were obtained with the calcination temperature at 800°C which is below the PbO evaporation temperature. This suggests that the combustion technique has the potential to reduce the calcined temperature.

The detail of how the sintering temperatures affect the crystal structure and morphology evolution of the PBZ ceramics, which is synthesized by the combustion method, has not been reported yet. Therefore, in the present work, the effect of firing temperatures on phase formation, microstructure and dielectric properties of PBZ ceramics prepared via a combustion method were studied.

Experimental

(Pb_{1-x}Ba_x)ZrO₃ (PBZ); $x = 0, 0.1$ and 0.2 , (PZ, PBZ10 and PBZ20), ceramics were synthesized via the combustion method using a thoroughly ground mixture of PbO, BaCO₃, ZrO₂ powders that were milled in the required stoichiometric ratio. The mixture of starting powders was milled and mixed in a ball mill, as well as wet homogenized with ethanol for 24 h using a zirconium grinding media. The suspensions were dried and the powders were ground using an agate mortar and sieved into a fine powder. After sieving, the mixed powders and urea were mixed in an agate mortar. Then, the mixtures of raw materials and the fuel, urea, were calcined at 800°C, for 1 h [15]. The PBZ powders were reground by wet ball-milling with a 2 wt.% binder. The calcined powders with binder were dried, crushed and sieved again. The calcined powder mixtures were isostatically pressed, at 80 MPa, into a pellet. Finally, the pellets were fired in a covered alumina crucible with a PbO atmosphere to prevent PbO loss at such a high firing temperature and sintered at 1150°C–1350°C for 3 h. The crystalline structure, microstructure and the phase transition of the PBZ were analyzed by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and a differential scanning calorimeter (DSC). The density of sintered pellets was measured using a liquid displacement method. The dielectric data were obtained measuring capacitance and loss tangent of fired silver pasted pellets.

Results and Discussion

Figure 1(a) shows the XRD patterns of the (Pb_{1-x}Ba_x)ZrO₃ (PBZ) powders which were calcined at 800°C for 1 h. It was found that the PBZ powders indexed in an orthorhombic structure. The intensity ratio of 004/240 peaks ($I_{004/240}$) and the relative intensity of superlattice reflections, namely 130/112, 210, 320/124 and 330/312, decreased with increasing Ba²⁺ content. It indicated that the replacement of Pb²⁺ by Ba²⁺ ions apparently influenced the orthorhombic structure.

Figure 1(b) shows the XRD pattern of PBZ ceramics sintered at 1250°C. The purity of the perovskite phase was found in all the sintered pellet samples. The diffraction lines of the PZ and PBZ10 ceramics were indexed with respect to orthorhombic structure. PBZ20 ceramics indexed with a rhombohedral structure. $I_{004/240}$ of PZ (~ 0.4) was higher than

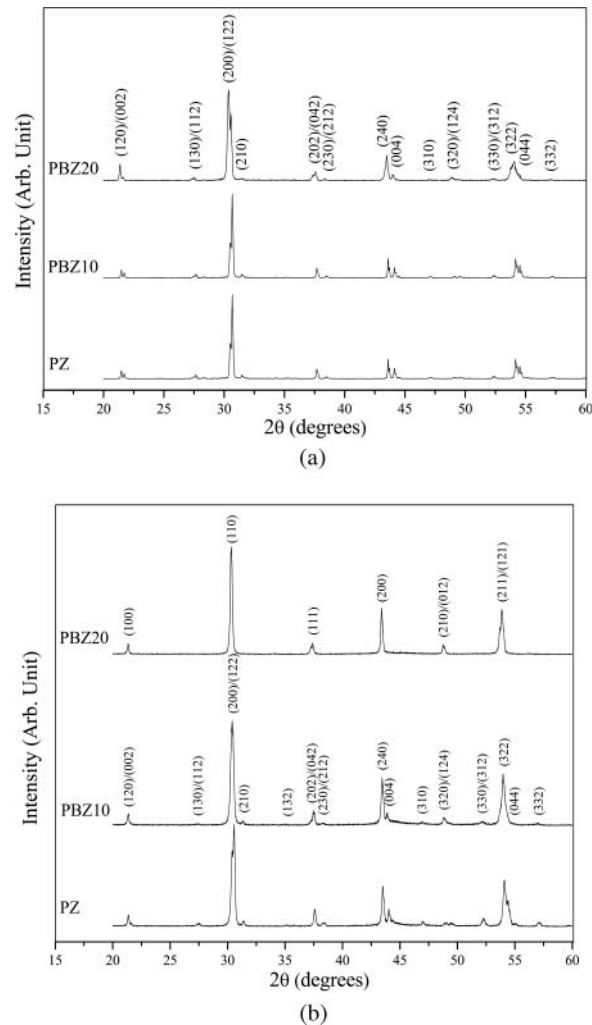


Figure 1. XRD patterns of (a) PBZ powders and (b) PBZ ceramics sintered at 1250°C.

PBZ10 (~ 0.3) which was similar to the previous study [8–14]. The sintering temperatures did not affect the phase formation of PBZ ceramics.

The scanning electron micrographs in Fig. 2 show the as-sintered and fractured surfaces of the PBZ10 ceramics. They exhibited well-developed grain size and dense microstructures. The pores were decreased with the increase of sintering temperatures. The average grain size tended to grow with the increase of sintering temperatures. The linear intercept method gave an average grain size which increased from 1.0 μm to 2.3 μm when the sintering temperatures increased from 1150°C to 1350°C (Table 1). The fracture surfaces of the sintered pellet samples each displayed inter-granular fractures in the case of low sintering temperatures. When the sintering temperatures increased the fracture surfaces showed intra-granular cleavage. This indicates that the grain boundaries were stronger with increasing sintering temperatures. These results were similar to PZ and PBZ20 ceramics.

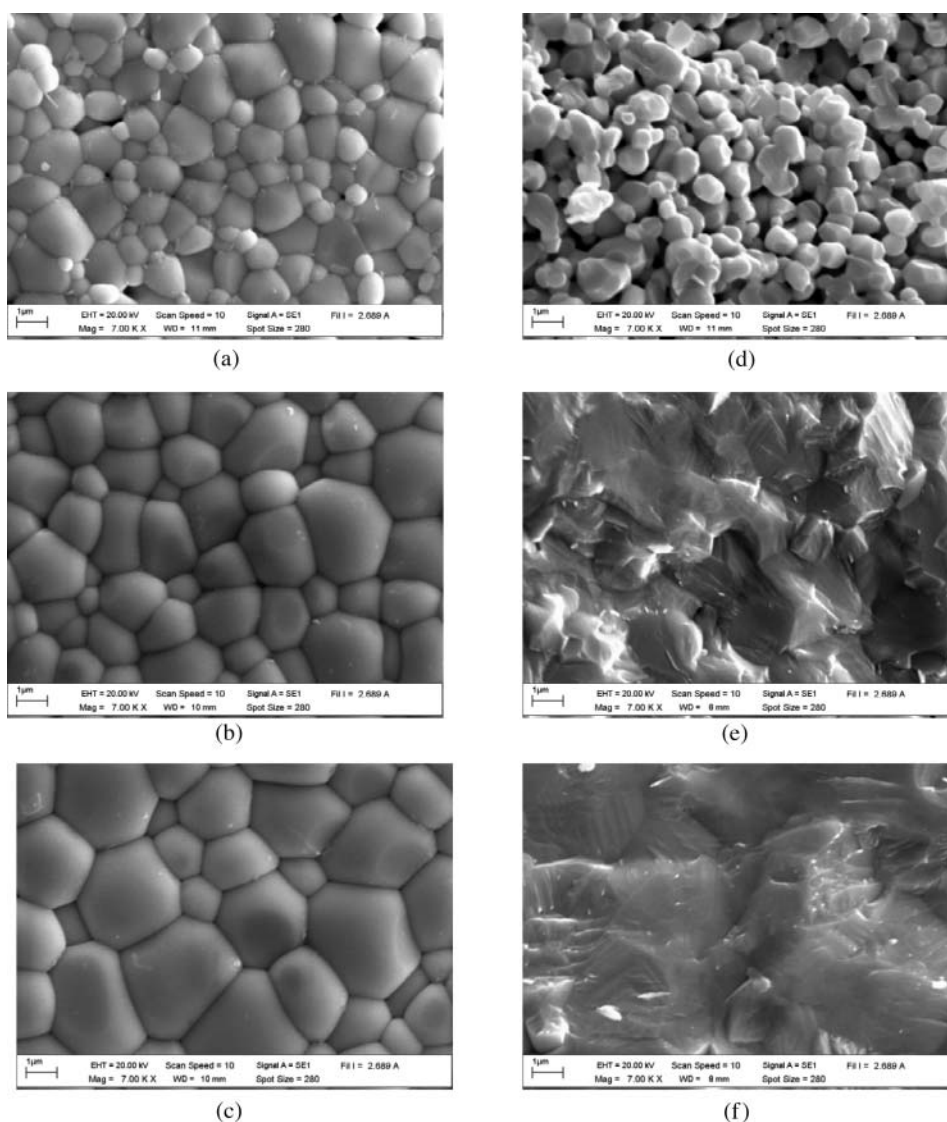


Figure 2. SEM micrographs of as-sintered surface of PBZ10 (a) sintered at 1150°C, (b) sintered at 1250°C, (c) sintered at 1350°C and fractured surfaces of PBZ10 (d) sintered at 1150°C, (e) sintered at 1250°C, (f) sintered at 1350°C.

However, at the same sintering temperature, the average grain size was decreased with increasing Ba^{2+} content as listed in Table 1.

The density of all x samples tended to increased with an increase in sintering temperatures, up to 1250°C, afterward density decreased with higher sintering temperatures (Table 1). At the same sintering temperature, the density was decreased with increased Ba^{2+} content. The results agreed with previous work [8–14]. The shrinkage was increased with the increasing sintering temperature up to 1300°C, and then decreased with higher sintering temperatures. Furthermore, at the same sintering temperatures, the shrinkage was

Table 1
Average grain size, Density and Shrinkage of PZ and PBZ ceramics

Sintered Temperature (°C)	PZ			PBZ10			PBZ20		
	Average grain size (μm)	Density (g/cm ³)	Shrinkage (%)	Average grain size (μm)	Density (g/cm ³)	Shrinkage (%)	Average grain size (μm)	Density (g/cm ³)	Shrinkage (%)
1150	1.1	7.89	14.6	1.0	7.61	14.6	0.5	7.32	10.6
1200	1.4	8.14	15.9	1.3	7.58	15.9	0.8	7.57	12.3
1250	2.6	8.27	16.7	1.6	7.75	16.7	1.2	7.69	14.6
1300	2.8	8.12	17.2	1.7	7.68	17.2	1.3	7.38	15.7
1350	3.0	7.88	16.9	2.3	7.63	16.6	1.4	7.33	15.0

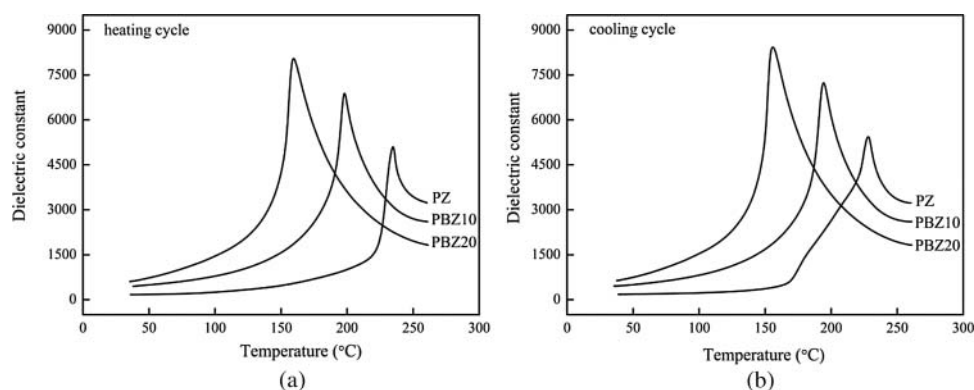


Figure 3. Dielectric constant versus temperature (a) on heating and (b) in cooling cycle.

decreased with increased Ba^{2+} . Higher Pb^{2+} content lead to a higher loss of lead and greater shrinkage was the result.

The PBZ ceramics sintered at 1250°C obtained the highest density, and were selected to study dielectric properties and DSC measurement. Figure 3 depicts the variation of the dielectric constant with temperature during heating and cooling of the PBZ samples for $0 \leq x \leq 0.2$. On the heating cycle, by replacing lead with barium, the dielectric maximum of PBZ ceramics was shown to shift to a lower temperature (Fig. 3(a)). The dielectric maximum was found around 235, 198 and 159°C for PZ, PBZ10 and PBZ20 ceramics. The dielectric maximum on heating in all samples is linked with the transition of the FE phase into the PE phase. In the cooling cycle, the specimens of PZ ceramics showed two dielectric anomalies around 228°C and 175°C which corresponded to the PE to FE and the FE to AFE phase transitions (Fig. 3(b)). The dielectric anomaly of the AFE to FE phase transition temperature during heating has not been observed by most researchers. The intermediate FE phase of PZ ceramics existing only in the cooling cycle agrees with previous works [8–11]. The maximum dielectric constant increases with increasing Ba^{2+} . For PBZ10 and PBZ20 ceramics, on the cooling cycle, dielectric anomalies were observed around 194°C and 155°C which corresponded to the PE to FE phase transition. The FE to AFE phase transition was not found in the dielectric peaks of PBZ10 and PBZ20 ceramics.

Figure 4 shows the DSC results of PBZ sintered samples. On the heating cycle, PZ had two endothermic peaks. The first endothermic peak $\sim 229^\circ\text{C}$ corresponded to the transformation from the AFE to FE phase; the secondary peak $\sim 232^\circ\text{C}$ related to the transition phase from FE to PE (Fig. 4(a)). The PBZ10 and PBZ20 ceramics were found to have only one endothermic peak at around 194°C and 154°C , when it was transforming from the FE to PE phase. In the cooling cycle, the PZ ceramics had two exothermic peaks at 229°C and 199°C , when they were transforming from PE to FE and FE to AFE phases (Fig. 4(b)). PBZ10 and PBZ20 ceramics showed only one exothermic peak when transforming from the PE-FE phase at 194°C and 150°C . The AFE to FE phase transition of the PZ ceramics during the heating cycle was observed from the DSC peak but not demonstrated in a dielectric measurement. This suggested that in the detection of a small anomaly of AFE to FE in phase transition, the DSC technique is more effective than the dielectric measurement.

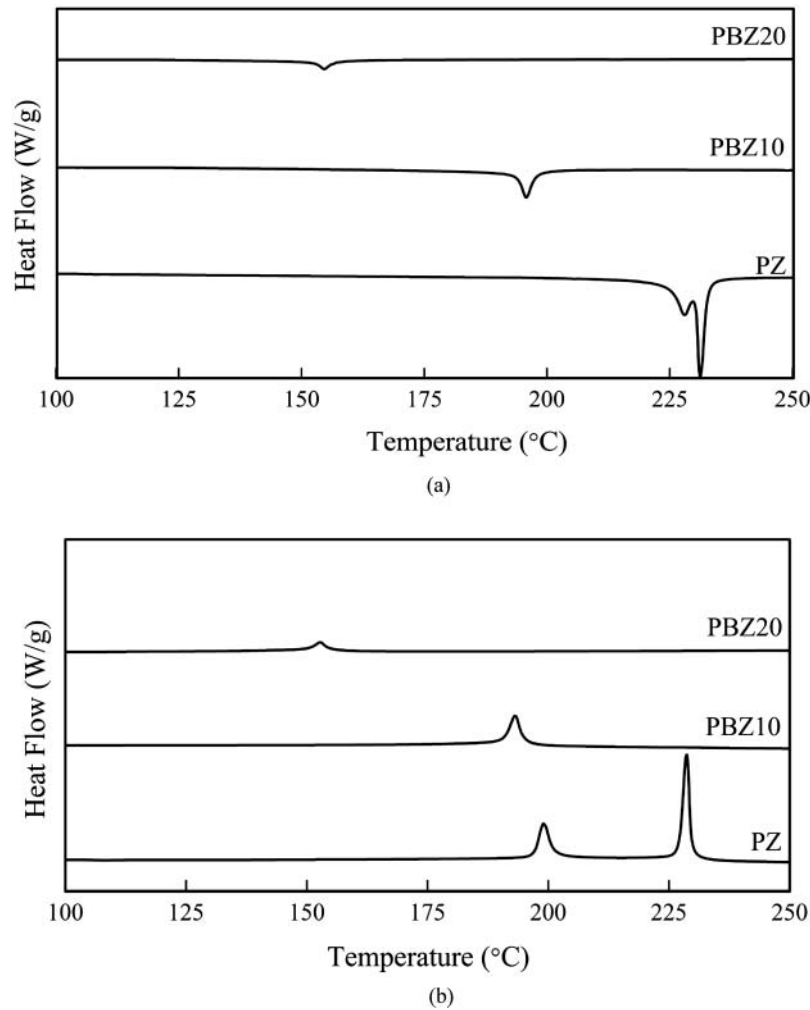


Figure 4. DSC thermograms of sintered samples (a) on heating cycle and (b) in cooling cycle.

Conclusions

We have for the first time demonstrated the synthesis of PBZ ceramics via the combustion technique. The Orthorhombic phase and the fraction of the antiferroelectric phase were found to decrease with increasing Ba^{2+} content. The Ba^{2+} content affected average grain size and grain boundaries hardness. They decreased with increasing Ba^{2+} content. The bulk density and shrinkage of PBZ ceramics continuously decreased with increasing Ba^{2+} content. Moreover, we also found the effect of sintering on average grain size and grain boundaries hardness, increased with increasing temperature. The maximum density was observed in the sample sintered at 1250°C . The maximum dielectric constant increased with increasing Ba^{2+} . The FE to PE and PE to FE phase transition temperatures were detected in all Ba^{2+} content. It progressively decreased with increasing Ba^{2+} content. AFE to FE and FE to AFE phase transitions were only detected in the PZ ceramics.

Acknowledgments

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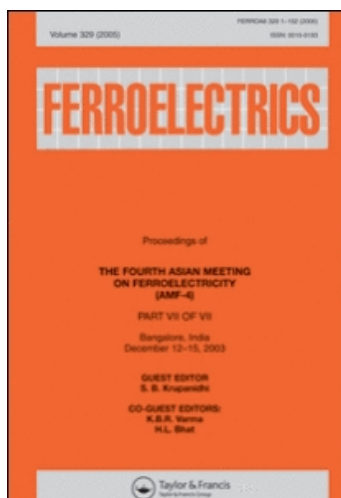
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Dependence of Firing Temperatures on Phase Formation, Microstructure and Phase Transition of (Pb_{1-x}Ba_x)TiO₃ Ceramics

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Dependence of Firing Temperatures on Phase Formation, Microstructure and Phase Transition of $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ Ceramics

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$(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ or PBT ($0.025 \leq x \leq 0.100$) ceramics were prepared via the solid state reaction method. The powders, calcined above 800°C , belonged to a pure tetragonal structure. The c/a ratio of the PBT powders decreased while the average particle size increased with the increasing of calcination temperatures. At the same calcination temperature, the average particle size increased when the Ba ion contents increased. A pure tetragonal structure was found in all PBT ceramics. The densest was discovered in the sample sintered at 1150°C in all compositions. The Curie temperature slightly decreased when the amount of Ba ions increased. The phase transition and dielectric constant were also measured.

Keywords Solid state reaction; tetragonality; calcination temperature; Curie temperature

Introduction

PbTiO_3 (PT) is one of the most interesting and most studied perovskites possessing a ferroelectric phase under ambient conditions. The strong interest in this material is caused by its high spontaneous polarization and the wide temperature stability of the ferroelectric phase. PT is used in the field of pyroelectric infrared detectors because of its large pyroelectric coefficient and low permittivity and is also a good material for sensors and actuators [1]. Unfortunately, pure PT, because of its high c/a ratio, has been difficult to synthesize as a mechanically robust, high density and monolithic ceramic [2]. However, the dense PT ceramics can be prepared by the substitution of a small amount of dopant, such as isovalent (Ca^{2+} , Ba^{2+} , Sr^{2+} , etc.) or off-valent (Sm^{3+} , Gd^{3+} , Nd^{3+} , etc.) ions into the Pb^{2+} sites. The lattice anisotropy will be decreased and the samples become hard and dense [3–5].

The $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ (PBT) ceramics were prepared by the substitution with small amounts of Ba ions into the Pb ion site. The substitution of Ba^{2+} for Pb^{2+} increases the lattice parameter a while decreasing the lattice parameter c . The cell parameters continuously, but nonlinearly, change with x . [2, 6]. The addition of a Ba ion not only reduced the lattice anisotropy but also maintained the excellent dielectric and piezoelectric anisotropy properties of the PBT ceramics, making it suitable for non-volatile random access memory

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(NVRAM) and surface acoustic wave (SAW) [7, 8]. The PBT ceramics can be synthesized by several methods and has been widely reported [9, 10]. Yang and Haile [9] prepared PBT via a sol-gel process. A high purity of $(\text{Pb}_{0.5}\text{Ba}_{0.5})\text{TiO}_3$ powder was obtained at 500°C with a nano-metric size about 30–50 nm and a specific surface area of $21.91 \text{ m}^2/\text{g}$. The particle size of the PBT powders fabricated via the polymeric citrate precursor route were found and ranged between 50 and 54 nm, in all compositions [10].

However, the effects of the addition of small amounts of Ba ions in PT on the phase and morphology evolutions have not been reported yet. Furthermore, the result of firing conditions on phase formation and the microstructure of $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ ceramics are not clearly understood. Therefore, in this present study, the $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ ($0.025 \leq x \leq 0.100$) ceramics were fabricated by the solid state reaction method. The structural phase and microstructure of the samples were studied as a function of firing conditions. In addition, the DSC result and phase transition were also investigated.

Experimental

$(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ or PBT ($0.025 \leq x \leq 0.100$) ceramics were prepared by the solid-state reaction method. The starting materials (PbO , BaCO_3 and TiO_2) were weighed, mixed and

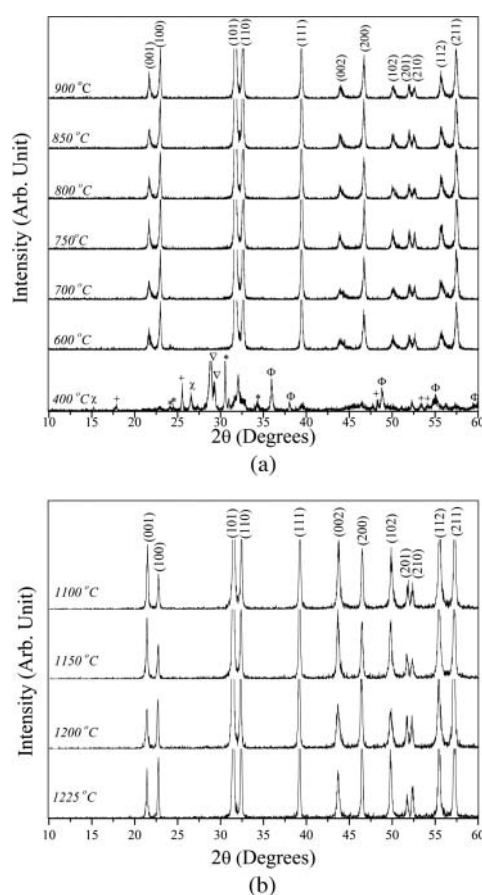


Figure 1. XRD patterns of PBT25; (a) powders calcined at various temperatures and (b) ceramics sintered at different temperatures: (X) TiO , (+) TiO_2 , (*) BaCO_3 , (∇) PbO_2 and (Φ) PbO .

ball-milled for 24 h by the zirconia media in ethyl alcohol. After being dried, the powders were ground in an agate mortar. The mixed powders were calcined at different temperatures (400–900°C) for 4 h in a covered alumina crucible. The PBT calcined powders were pressed into the pellets with a diameter of 15 mm. The pellets were then sintered at temperatures ranging from 1100–1225°C for 2 h. The phase identification of the calcined powders and sintered ceramics were carried out through an X-ray diffractometer. The microstructures were investigated via a scanning electron microscope (SEM). The density of the sintered pellets was measured using the Archimedes method. Silver electrodes were coated on both sides of the polished samples. The room temperature dielectric constant was then measured

Table 1

The percent perovskite phase, lattice parameter a , c , c/a ratio and particle size of PBT powders

Ba ²⁺ contents (%)	Calcination temperatures (°C)	% perovskite phase	Lattice parameter (Å)		c/a ratio	Average particle size (μm)
			a	c		
2.5	400	8.39	—	—	—	0.13
	600	93.16	3.884	4.132	1.064	0.16
	700	95.12	3.884	4.128	1.063	0.24
	750	96.90	3.887	4.127	1.062	0.30
	800	100	3.888	4.124	1.061	0.39
	850	100	3.889	4.121	1.060	0.43
	900	100	3.890	4.114	1.058	0.62
5.0	400	7.65	—	—	—	0.14
	600	94.51	3.885	4.128	1.063	0.19
	700	97.33	3.886	4.125	1.062	0.24
	750	98.65	3.886	4.124	1.061	0.32
	800	100	3.887	4.123	1.061	0.43
	850	100	3.889	4.121	1.060	0.60
	900	100	3.890	4.120	1.059	0.77
7.5	400	9.45	—	—	—	0.14
	600	91.85	3.887	4.115	1.059	0.20
	700	93.42	3.887	4.114	1.058	0.25
	750	96.54	3.888	4.111	1.057	0.33
	800	100	3.891	4.110	1.056	0.44
	850	100	3.891	4.108	1.056	0.59
	900	100	3.894	4.108	1.055	0.65
10.0	400	9.87	—	—	—	0.14
	600	89.90	3.884	4.132	1.064	0.21
	700	94.67	3.887	4.129	1.062	0.25
	750	98.69	3.889	4.126	1.060	0.34
	800	100	3.890	4.122	1.060	0.45
	850	100	3.891	4.120	1.059	0.56
	900	100	3.893	4.117	1.058	0.74

by a LCR meter. The Curie temperature (T_c) of PBT ceramics was evaluated using a differential scanning calorimeter (DSC).

Results and Discussion

Figure 1(a) shows the XRD patterns of $(\text{Pb}_{0.975}\text{Ba}_{0.025})\text{TiO}_3$ (PBT25) powders with different synthesis conditions. The X-ray analysis indicated that the PBT25 powders, calcined from 600 to 900°C, have mainly set peaks with a major peak at (101). All of them belong to the tetragonal phase of a perovskite-type structure and matched with JCPDS file number 06-0452 [11]. For PBT powders calcined below 800°C, impurity phases such as PbO , BaCO_3 , TiO_2 , PbO_2 , and TiO were formed. Above 800°C of calcination temperature, the impurity phases disappeared and the pure tetragonal phase was discovered in all samples. The XRD results of $(\text{Pb}_{0.950}\text{Ba}_{0.050})\text{TiO}_3$ (PBT50), $(\text{Pb}_{0.925}\text{Ba}_{0.075})\text{TiO}_3$ (PBT75) and $(\text{Pb}_{0.900}\text{Ba}_{0.100})\text{TiO}_3$ (PBT100) were similar with PBT25.

The relative amounts of the perovskite phase were calculated by measuring the major XRD peak intensities of the perovskite phase. The percentage of perovskite phase is described by the following equation:

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{PbO}} + I_{\text{BaCO}_3} + I_{\text{TiO}_2} + I_{\text{PbO}_2} + I_{\text{TiO}}} \right) \times 100$$

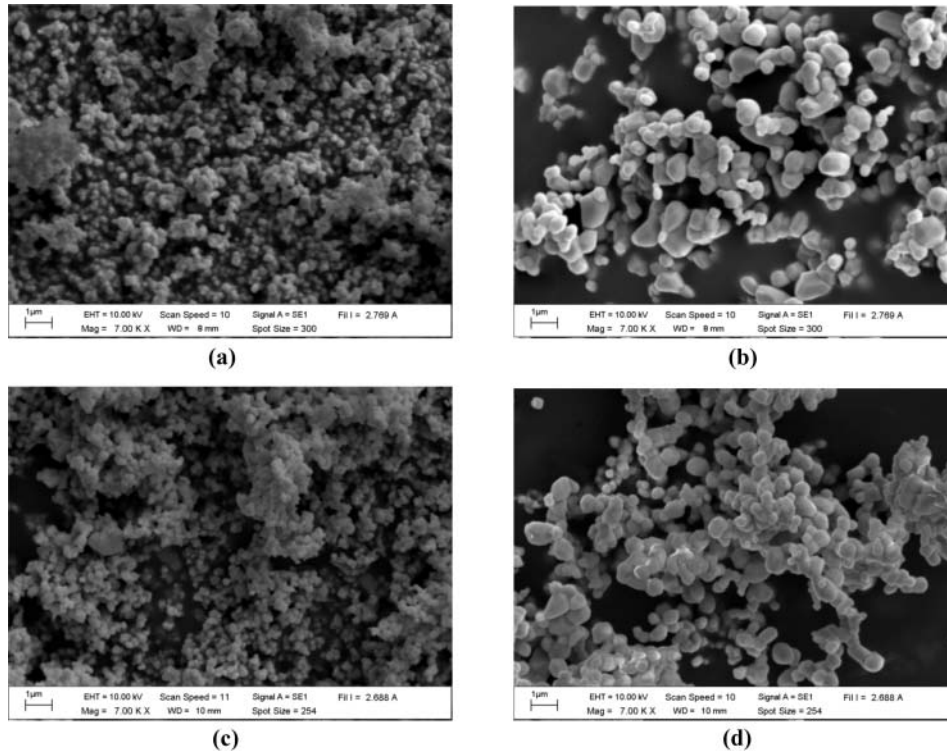


Figure 2. SEM micrographs of the PBT powders: (a) PBT50 calcined at 600°C, (b) PBT50 calcined at 900°C, (c) PBT100 calcined at 600°C and (d) PBT100 calcined at 900°C.

This equation is a well-known equation widely employed in connection with the preparation of complex perovskite structure materials [12, 13]. Where I_{perov} , I_{PbO} , I_{BaCO_3} , I_{TiO_2} , I_{PbO_2} and I_{TiO} refer to the intensity of the (101) perovskite peak, and the intensities of the highest PbO, BaCO₃, TiO₂, PbO₂ and TiO, respectively. The percent perovskite phase of PBT powders in all compositions at various calcination temperatures are shown in Table 1. There was an increase in the phase purity with increasing calcination temperatures.

The lattice parameters and tetragonality (c/a) of the PBT powders in all compounds at different temperatures (600–900°C) were computed from the (100), (001), (200) and (002) reflective peaks of the XRD patterns and are listed in Table 1. The lattice parameter c and c/a ratio decreased while the lattice parameter a increased with the increasing of the calcination temperatures.

The powders calcined at 800°C were pressed into pellets and sintered from 1100 to 1225°C. Figure 1(b) demonstrates the XRD patterns of the PBT25 sintered pellets at various sintering temperatures. The single tetragonal perovskite phase of PBT was obtained in all compositions. This result was similar with the XRD results of PBT50, PBT75 and PBT100 and indicated that Ba forms a complete solid solution with $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ in the studied composition range. The c/a ratio tended to slightly decrease with the increase of Ba ion contents. There is a decrease in the tetragonality of the PBT sample, compared to the PT, due to the incorporation of a smaller Ba ion in the place of the Pb ion site.

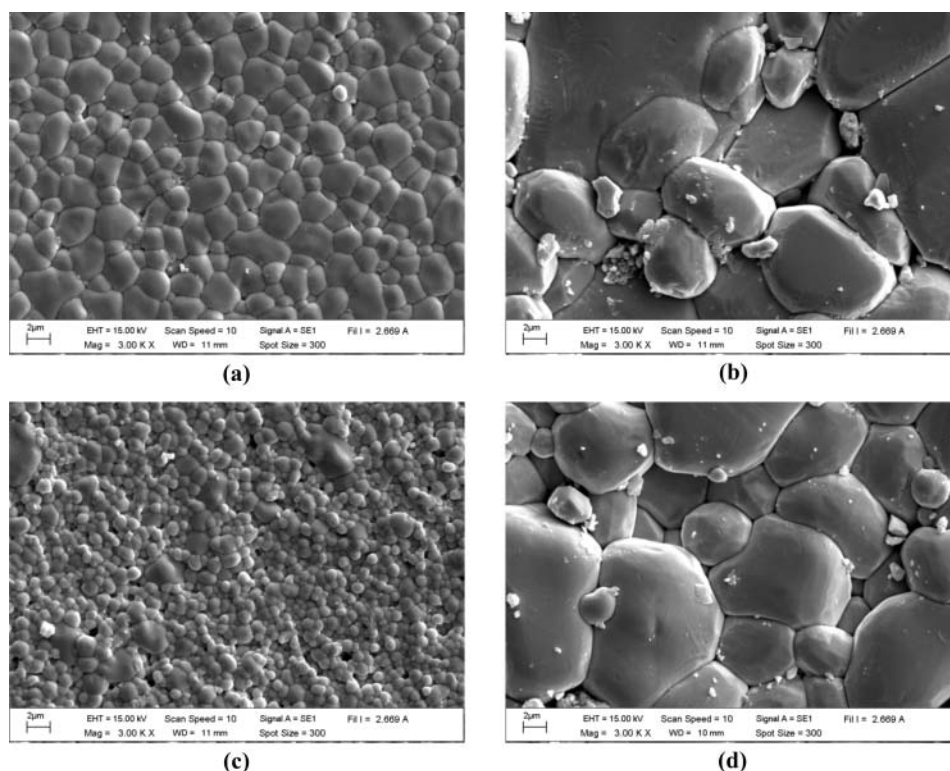


Figure 3. SEM micrographs of the PBT ceramics: (a) PBT25 sintered at 1100°C, (b) PBT25 sintered at 1225°C, (c) PBT75 sintered at 1100°C and (d) PBT75 sintered at 1225°C.

Figure 2 shows the SEM morphology of synthesized PBT powders with different temperatures for 4 h. The synthesized PBT powders consisted of ultra-fine particulates. The particles were highly agglomerated and basically irregular in shape, with a substantial variation in particle size. The powders sintered above 800°C seemed to display a significant level of necking and bonding as if they were in the initial stages of sintering. The obtained particle size of PBT powders increased as the calcination temperatures increased (Table 1). Figure 3 demonstrates the SEM micrographs of PBT ceramics sintered at various temperatures. The grain size tended to increase when the sintering temperatures increased (Table 2).

The densest of the PBT ceramics, in all compounds, were obtained in ceramics sintered at 1150°C as shown in Table 2. The density of the samples increased up to a maximum value of 7.438, 7.310, 7.419 and 7.444 g/cm³ in samples with $x = 0.025, 0.050, 0.075$ and 0.100, respectively; then the value decreased with the increase in the sintering temperature. The density decreased when the temperature was higher than the optimal temperature. This is because there is a compromise between grain growth and the densification mechanisms during heat treatment, especially during the final stage of sintering. If the sintering rate is too fast and/or if the temperature is too high, the grain growth mechanism is faster than the densification [14].

The tendency of the room temperature dielectric constant decreased, while the grain size tends to increased with the increasing of the sintering temperatures as seen in Table 2. Similar results were reported in BaTiO₃, modified PbTiO₃, Pb_{0.9}La_{0.1}TiO₃ and Pb(Zr_{0.52}Ti_{0.48})O₃ ceramics [15–18]. Kakegawa *et al.* described the decrease of the dielectric constant may due to the changing of the chemical composition [18]. In this

Table 2
The c/a ratio, average grain size, density and dielectric constant of PBT ceramics

Ba ²⁺ contents (%)	Sintering temperatures (°C)	c/a ratio	Average grain size (μm)	Density (g/cm ³)	dielectric constant at room temperature
2.5	1100	1.059	1.9	7.132	2348
	1150	1.060	1.8	7.438	1197
	1200	1.059	2.6	7.432	1131
	1225	1.059	5.1	7.412	708
5.0	1100	1.057	1.5	7.282	3151
	1150	1.057	2.0	7.310	1394
	1200	1.057	2.1	7.296	1077
	1225	1.058	8.4	7.235	866
7.5	1100	1.057	0.9	7.343	2550
	1150	1.056	3.0	7.419	1922
	1200	1.057	6.4	7.417	1432
	1225	1.056	5.7	7.412	912
10.0	1100	1.055	1.0	6.983	944
	1150	1.055	2.0	7.444	938
	1200	1.056	7.1	7.405	876
	1225	1.056	4.9	7.280	294

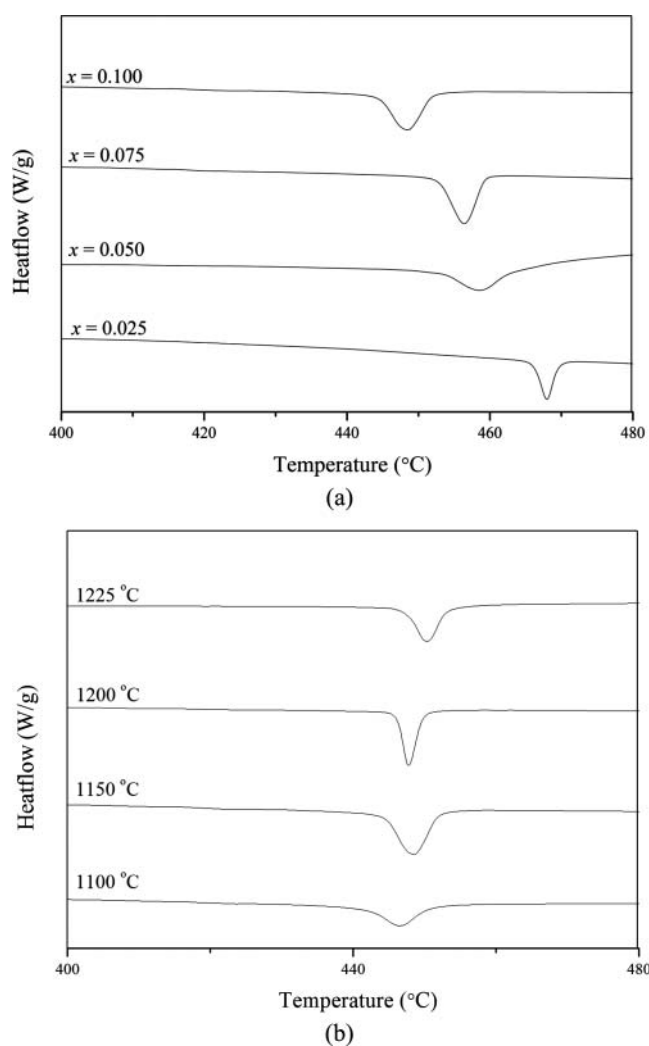


Figure 4. The DSC traces of: (a) PBT pellets sintered at 1150°C with various x and (b) PBT100 pellets with different sintering temperatures.

study, the higher sintering temperature led a greater lead loss, which evaporated above 800°C [19].

The ceramics which were sintered at 1150°C and PBT100 ceramics with different sintering temperatures were selected to study phase transition by DSC measurement. Figure 4(a) shows the DSC graph of PBT ceramics with different x . The endothermic peak associated with the Curie temperature (T_c)—the transition temperature from ferroelectric (FE) to paraelectric (PE) phase—were observed. The T_c was decreased with an increase of Ba ion content. The T_c of PBT ceramics were found to be 468, 459, 457 and 447°C for samples with $x = 0.025, 0.050, 0.075$ and 0.100 , respectively. The DSC patterns of PBT100 ceramics with different temperatures are demonstrated in Fig. 4(b). The T_c tended to slightly increase with an increase of sintering temperatures. The T_c of PBT100

ceramics were 446, 447, 449 and 450°C for samples sintered at 1100, 1150, 1200 and 1250°C, respectively. These results agreed with previous work [20].

Conclusions

The firing temperatures and Ba ion contents have a strong influence on the phase formation, morphology, lattice parameter and tetragonality of PBT ceramics. The pure tetragonal perovskite phase appeared above 800°C of calcination temperature. The tetragonality of powders decreased with an increase of calcination temperatures. The particles have a spherical form and tend to increase with the rising of temperatures. The densest of the PBT pellets was observed in ceramics sintered at 1150°C in all compositions. The T_c of the PBT ceramics depended on the sintering temperatures and Ba ion contents.

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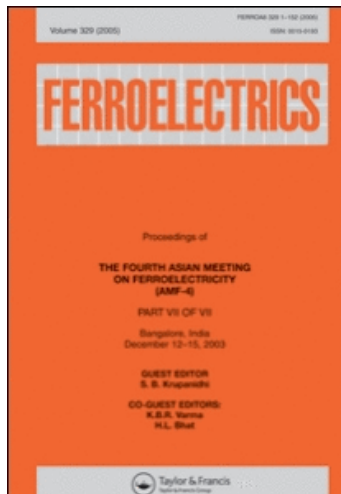
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Preparation of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Ceramics via the Solid State Reaction Method

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Preparation of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Ceramics via the Solid State Reaction Method

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The effect of calcination (1000–1400°C), sintering temperatures (1400–1650 °C) and the changing of ions in A and B sites on the phase formation and microstructure of barium strontium zirconate titanate $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, BSZT, $x = 0.25$ and 0.50 ceramics were investigated. BSZT powders were prepared by the solid state reaction method. It was found that BSZT samples indexed in a cubic structure. Higher calcination temperatures increased the percentage of the perovskite phase. The pure perovskite phase of BSZT with $x = 0.25$ was detected above the calcined temperature at 1400°C. For the $x = 0.50$, the second phase of BSZT with $x = 0.25$ was found at all calcination temperatures. The purity phase was detected in all the ceramic samples. At the same sintering temperatures, the lattice parameter of BSZT ceramics with $x = 0.50$ has higher than with $x = 0.25$. The microstructure of the BSZT powders exhibited an almost-spherical morphology and had a porous agglomerated form. The average particle size (160–420 nm) and average grain size (0.68–12.45 μm) increased with the increase in calcination and sintering temperatures. The optimized density, around 5.64 and 5.42 g/cm^3 for $x = 0.25$ and 0.50 , were obtained from BSZT samples calcined at 1500 and 1550°C for 2 h.

Keywords Cubic perovskite; barium strontium zirconium titanate; microstructure; phase formation

Introduction

Barium titanate (BaTiO_3) has been extensively studied due to its interesting properties such as a high dielectric constant in the structure phase transition which transferred between the paraelectric (cubic) and ferroelectric (tetragonal) phase and showed a dielectric peak (ϵ_{max}) at around 130 °C [1]. To enhance these properties, BaTiO_3 was modified with Sr^{2+} and Zr^{4+} , by substituting the Ba^{2+} ion with a Sr^{2+} ion which will shift the T_c of BaTiO_3 close to room temperature [2] and by substituting the Ti^{4+} ion with a Zr^{4+} ion which will reduce the dielectric loss, be chemically more stable, and reduce leakage current in the BaTiO_3 -based materials [3].

$(\text{Ba},\text{Sr})(\text{Zr},\text{Ti})\text{O}_3$ powders have been prepared by the sol-gel technique [4, 5] but this form of processing sample preparations is complex and expensive [6]. Alternatively, the solid-state reaction method is probably one of the most fundamental, practical and

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routine methods which has been used, developed and modified in both scientific research and industrial mass production for many years [7, 8]. Our previous work prepared and characterized $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics with $x = 0.75$ [9]. The pure phase was obtained at a calcined temperature of 1350°C and a maximum density of around 5.42 g/cm^3 was found in the sample sintered at 1550°C . The literature survey has revealed that paraelectric $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$; $x \geq 0.2$ ceramics were chemically more stable, had a lower transition temperature (T_c) and had a high dielectric constant [10], which is suitable for applications in microwave dielectric resonators and miniature resonating devices used in microwave integrated circuits [11]. However, $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$; $x = 0.25$ and 0.50 ceramics have not been reported in the literature. So, in this work, the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$; BSZT, $x = 0.25$ and 0.50 ceramics were studied via the solid-state reaction method. The effect of calcination, sintering temperatures, and the replacing of ions in the A and B sites in the phase formation and microstructure of BSZT ceramics were also investigated.

Experimental

The starting materials were commercially available: BaCO_3 (99%), SrCO_3 (99%), ZrO_2 (99%) and TiO_2 (99%). Barium strontium zirconate titanate $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$; $x = 0.25$ and 0.50 powders were prepared via the solid-state reaction method by thoroughly grinding mixtures of the raw materials by a ball milling procedure (zirconia milling media under ethanol for 24 h). Drying was carried out at 120°C for 4 h. After sieving, the mixing powders were calcined at temperatures ranging from 1000 to 1400°C , with a dwell time of 4 h and a heating/cooling rate of 5°C/min . The calcined powders were mixed with a binder and ground by ball milling with ethanol again for 24 h to deagglomerate. The granulated powders were placed into disks with a diameter of 15 mm and pressed at a pressure of 80 MPa to form a green disk. These disks were sintered in a crucible from 1400 to 1650°C for 2 h and cooled in a furnace. X-ray diffraction was employed to identify the phases formed and the optimum temperature for the pure crystal structure in the BSZT powders and ceramics. The calcined powders and sintered ceramics morphologies were imaged using scanning electron microscopy. The density of the sintered ceramics was measured by the Archimedes method. The average particle size and the average grain size were determined by using a mean linear intercept method.

Results and Discussion

Figure 1 (a) shows the XRD patterns of the BSZT powders of $x = 0.25$ with different synthesis conditions. They were indexed on the basis of a cubic structure matched with JCPDS file number 31-0174. The impurity phases of BaO , BaCO_3 , TiO_2 and BaZrO_3 were observed when calcination temperatures were below 1400°C . The pure cubic perovskite phase was detected in powders calcined higher than 1400°C . The percentage of the perovskite phase was calculated with the equation (1), which is a well-known equation widely employed in connection with the preparation of complex perovskite structure materials [9]. Here I_{perov} , I_{BaO} , I_{BaCO_3} , I_{TiO_2} and I_{BaZrO_3} refer to the intensity of the (101) perovskite peak, intensities of the highest BaO , BaCO_3 , TiO_2 peaks and BaZrO_3 , respectively.

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{BaO}} + I_{\text{BaCO}_3} + I_{\text{TiO}_2} + I_{\text{BaZrO}_3}} \right) \times 100 \quad (1)$$

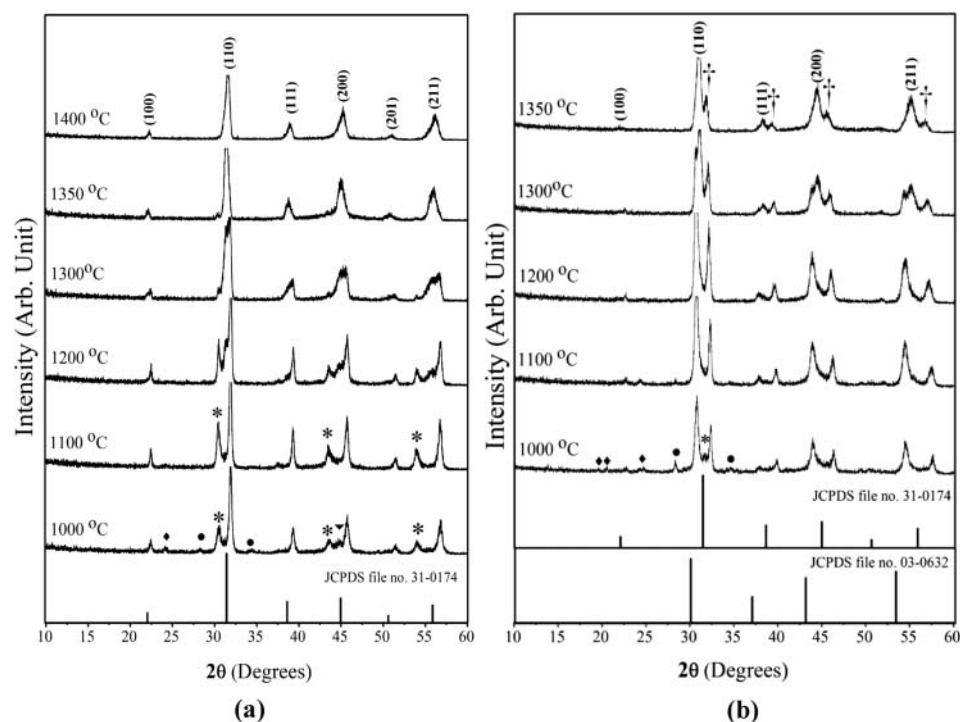


Figure 1. (a) XRD patterns of BSZT powders with $x = 0.25$ calcined between 1000 and 1400°C, (b) XRD peaks of BSZT powders with $x = 0.50$ calcined between 1000 and 1350°C for 4 h: (●) BaO; (◆) BaCO₃; (▼) TiO₂; (*) BaZrO₃ (†) BSZT ($x = 0.25$).

The percent of the perovskite phase of BSZT calcined powders with $x = 0.25$ are listed in Table 1. An increase of phase purity with increasing calcination temperatures was evident. The XRD trace of $x = 0.50$ calcined between 1000 and 1350°C is shown in Fig. 1 (b). The phase formation of $x = 0.50$ was indexed on the basis of the cubic structure

Table 1
Percent perovskite phase and average particle size of BSZT calcined powders

Calcined temperature (°C)	$x = 0.25$		$x = 0.50$	
	Percent perovskite phase (%)	Average particle size (nm)	Percent perovskite phase (%)	Average particle size (nm)
1000	69.7	190	49.9	160
1100	73.5	200	54.2	190
1200	77.1	280	59.7	260
1300	95.3	320	60.5	270
1350	98.5	380	72.3	300
1400	100	420	67.9	360

which matched with JCPDS file number 03-0632, as shown in Fig. 1 (b). The impurity phases of BaO, BaCO₃ and BaZrO₃ were observed when calcination temperatures were below 1350°C. In addition, the second phase of BSZT with $x = 0.25$, which matched with JCPDS file number 31-0174, was found at all calcination temperatures. The percentage of the perovskite phase was calculated and is shown in Table 1. The highest percent perovskite phase of BSZT calcined powders with $x = 0.50$ was obtained from the powder calcined at 1350°C.

Figure 2 (a), (b), (c) and (d) illustrate the SEM photographs of morphological changes in the calcined BSZT powders with $x = 0.25$ and 0.50. In general, the particles are agglomerated and spherical in shape with variation in particle size. As calcination temperatures increased from 1000 to 1400°C, the increased average particle size was between 190 and 420 nm for $x = 0.25$ and from 160 to 360 nm for $x = 0.50$ as displayed in Table 1. In each condition of calcined temperature, the average particle size of the $x = 0.25$ was slightly larger than the $x = 0.50$.

The calcined powders with the $x = 0.25$ and 0.50 obtained at 1400 and 1350°C were formed into disks, pressed into pellets, and sintered from 1400 to 1650°C for 2 h. Figure 3 (a) and (b) shows the XRD patterns of the BSZT sintered ceramics with $x = 0.25$ and 0.50. All samples, of both compositions, were indexed as a single phase with a perovskite cubic structure. It may be noted that the second phase which occurred in calcined powders disappeared during the sintering process. The phase formation of $x = 0.25$ and 0.50 correlated and matched with JCPDS file number 31-0174. The lattice parameter a as a function of sintering temperatures is shown in Table 2. The lattice parameter a increased with the increasing of sintering temperatures. At the same sintering temperatures, the lattice parameter a of BSZT ceramics with $x = 0.50$ was higher than $x = 0.25$. The changing of sintering temperatures and the ions in the A and B sites affected the lattice strain, which is determined by the change in the d spacing and the lattice parameters of the samples [12] and resulted in a change in lattice parameter a . Furthermore, the reflection peaks were sharper with higher sintering temperatures, indicating larger crystallization when the sintered temperature increased.

The morphological changes in the BSZT surface of the sintered ceramics with $x = 0.25$ and 0.50 as a function of sintered temperatures are shown in Fig. 2 (e), (f), (g) and (h). It was evident that the porosity decreased, but the average grain sizes increased from 0.94–12.45 μm for $x = 0.25$ and from 0.68–10.66 μm for $x = 0.50$ when the sintering temperatures increased from 1400 to 1650°C as shown in Table 2. In each sintering temperature, the average grain size of the $x = 0.25$ had more than the $x = 0.50$ in value. The increase of grain size obtained from the SEM images corresponded to the XRD result.

The density of BSZT ceramics with the $x = 0.25$ and 0.50, as a function of the different sintering temperatures, is shown in Table 2. The density first increased and reached its highest at 1500 and 1550°C for $x = 0.25$ and 0.50 then dropped in value when the sintering temperature was higher than 1500 and 1550°C, respectively. Thus, the optimal sintering temperature of highly dense BSZT samples of 5.64 and 5.42 g/cm³ of the $x = 0.25$ and 0.50 was obtained. The density decreased when the temperature was higher than the optimum temperature in the sintering process. The grain growth correlates with the densification mechanisms during treatment, particularly during the final stage of sintering. The density of the sintered samples maybe decreased because of the expanding of trapped gases in the pores. The gas-fill pores assemble and grow because of grain growth [13, 14]. The percent of shrinkage of the pellet samples increased with the increase of sintering temperatures as shown in Table 2.

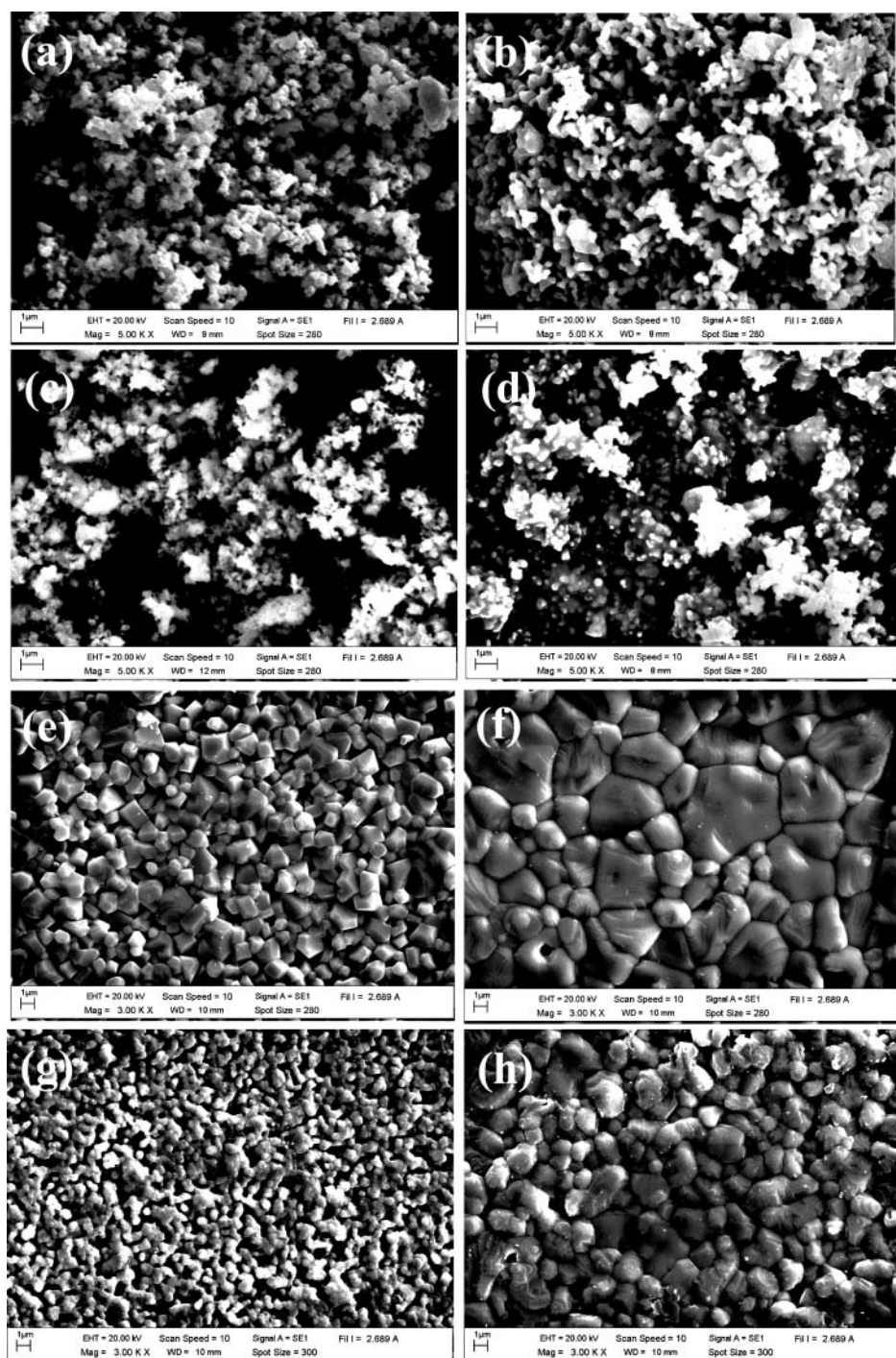


Figure 2. SEM photomicrographs of BSZT powders with $x = 0.25$ calcined at: (a) 1000°C, (b) 1350°C and $x = 0.50$ calcined at (c) 1000°C, (d) 1350°C for 4 h, the pellets surface of $x = 0.25$ sintered at: (e) 1400°C and (f) 1450°C for 2 h and $x = 0.50$ sintered at: (g) 1400°C and (h) 1450°C.

Table 2
Lattice parameter a , density, shrinkage and average grain size of BSZT sintered ceramics

Sintered temperature (°C)	$x = 0.25$				$x = 0.50$			
	Lattice parameter a (Å)	Average grain size (μm)	Density (g/cm^3)	Shrinkage (%)	Lattice parameter a (Å)	Average grain size (μm)	Density (g/cm^3)	Shrinkage (%)
1400	4.0193	0.94	5.08	14.13	4.0475	0.68	5.09	6.78
1450	4.0210	1.15	5.51	14.78	4.0475	0.92	5.24	15.02
1500	4.0216	1.57	5.64	14.88	4.0500	1.40	5.29	15.82
1550	4.0219	5.43	5.52	15.15	4.0517	5.17	5.42	16.15
1600	4.0227	8.61	5.56	15.54	4.0543	7.76	5.28	16.41
1650	4.0244	12.45	5.49	16.32	4.0578	10.66	5.01	16.67

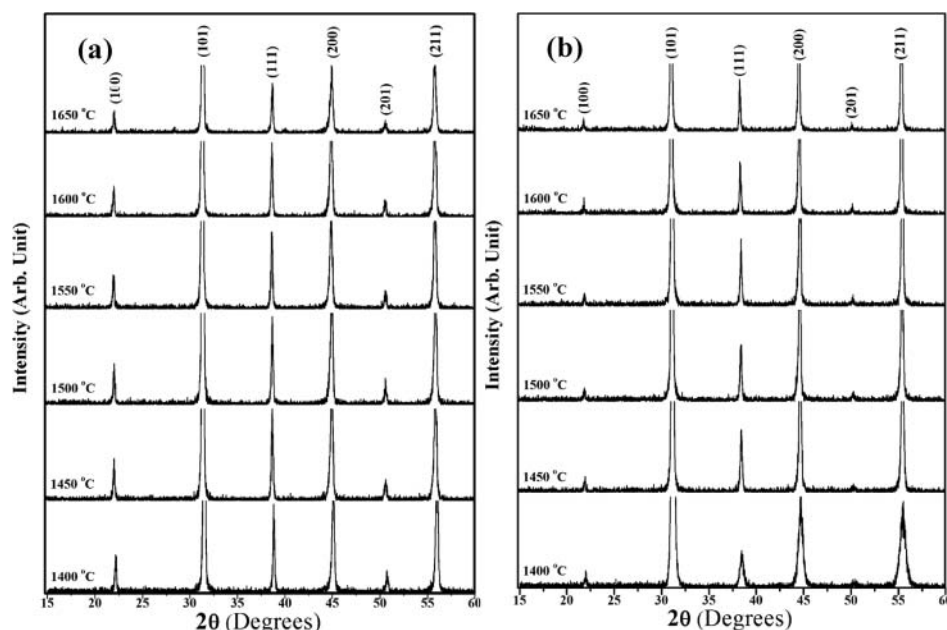


Figure 3. XRD patterns of BSZT ceramics with (a) $x = 0.25$ and (b) $x = 0.50$.

Conclusions

The pure cubic crystal and the maximum percentage of the perovskite phase (72.3%) of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ powders with $x = 0.25$ and 0.50 can be obtained by calcination at 1400 and 1350°C through the solid-state reaction method. The second phase found in BSZT powders with $x = 0.50$ disappeared in all sintered samples. BSZT ceramics in both compositions were identified as a single phase with a cubic perovskite structure. The average particle size and the average grain size increased with the increasing of calcination and sintering temperatures. A highest density of 5.64 and 5.42 g/cm^3 of the $x = 0.25$ and 0.50 content was obtained from the sintered ceramics at 1500 and 1550°C for 2 h . The crystallization, lattice parameter and homogeneity of the calcined and sintered samples had been influenced by the calcinations, sintering temperatures and the change of ions in the A and B sites.

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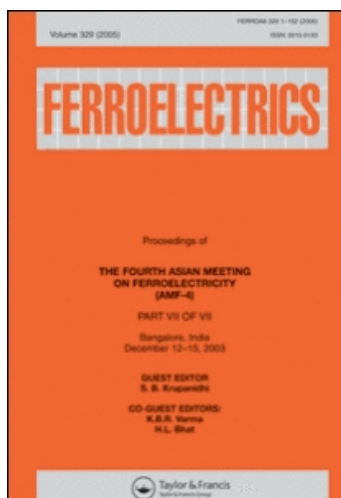
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The Effect of Excess PbO on Crystal Structure, Microstructure, Phase Transition and Dielectric Properties of $(\text{Pb}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$ Ceramics

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The Effect of Excess PbO on Crystal Structure, Microstructure, Phase Transition and Dielectric Properties of $(\text{Pb}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$ Ceramics

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This study investigated the effect of excess PbO on the crystal structure, microstructure, phase transition and dielectric properties of $(\text{Pb}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$ (PST25) ceramics. The PST25 ceramics were synthesized by the solid-state reaction method with various excess PbO levels (0, 1, 3, 5 and 10 wt.%). The excess PbO was added to compensate for the lead loss from evaporation during calcination and sintering at 950°C and 1150°C. The X-ray characterization revealed that all samples had a tetragonal structure and impurity phases since PbO and PbO_2 were detected in the calcined powders with higher than 3 wt.% of excess PbO. A pure perovskite phase was obtained in all ceramic samples. The c/a ratios tended to decrease with an increasing excess PbO in the calcined powders and sintered pellets. The average particle size and the average grain size of the PST tended to increase with an increase of PbO content. With 1 wt.% of excess PbO, the highest density and a broader dielectric peak were obtained. The dielectric spectrum was not present in the 3, 5 and 10 wt.% excess of PbO samples. The DSC results indicated that the Curie point shifted to a higher temperature with the increase in the excess of PbO until 3 wt.%, then slightly decreased with higher excess PbO.

Keywords Excess PbO; tetragonality; lead strontium titanate; phase transition

Introduction

Lead strontium titanate $[(\text{Pb}_{1-x}\text{Sr}_x)\text{TiO}_3]$ (PST) is a complete solid solution of PbTiO_3 (PT) and SrTiO_3 (ST) [1]. PST (where $0 < x < 1$) is highly suitable for electronic and micro-electronic applications such as: infrared sensors, nonvolatile memories, dynamic random access memory (DRAM), etc. [1–3]. Earlier studies indicated that the Curie temperature of PST varied from -220 to 490°C [1] and the composition range of the tetragonal/cubic phase boundary at room temperature was about $x \approx 0.50$ – 0.70 [4]. The phase diagram of a PST solid solution was studied by Nomura and Sawada [5, 6]. They found the exact phase transition from the tetragonal to cubic phase occurred at $x \approx 0.65$ at room temperature. The dielectric properties of PST ceramics were studied by Subrahmanyam and Goo. They reported that, for the ferroelectric tetragonal phase region, the maximum value of the dielectric constant (7,675) was found in the $x = 0.2$ sample. For the paraelectric cubic phase region, the maximum value of the dielectric constant (3,500) was found in the $x = 0.7$ sample [7].

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PST are prepared by various techniques such as: the coprecipitation method [1], the complex polymerization method [4], the precursor solution method [8] and the sol-gel method [9, 10]. All of these methods use high-purity inorganic or organic chemicals with homogeneity and a precise composition as starting materials but the production costs are high with little quantity synthesized. The conventional solid-state reaction method is more economical for large batch processing of these ferroelectric materials [11]. The literature survey showed that PST ceramics prepared by conventional methods which used high sintering temperatures above 1200°C [3, 6], suffered from the problem of PbO loss because of the low melting point of PbO which is about 850°C. This makes it difficult to achieve high densities and changes the intrinsic electromechanical properties of the materials [12, 13]. In order to compensate for the lead loss in the samples, some excess PbO is usually added during the batch preparation [14, 15]. Therefore, the effect of excess PbO on the crystal structure, microstructure, phase transition and dielectric properties of $(\text{Pb}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$ (henceforth called as PST25) ceramics synthesized by a solid-state reaction method was investigated in this study.

Experimental Procedure

The PST25 ceramics were prepared by a conventional solid-state reaction of lead oxide (99% PbO), strontium carbonate (98+% SrCO_3) and titanium oxide (99% TiO_2). The raw materials were ball milled with stabilized zirconia balls and ethanol for 24 h, and then calcined at 950°C for 2 h [16]. An excess of PbO, equivalent to 0, 1, 3, 5, or 10 wt.%, was added prior to ball milling. The calcined powders were then pressed into disks with a diameter of 15 mm at a pressure of 80 MPa. Subsequently, the pellets were sintered in a sealed alumina crucible at 1150°C for 3 h.

The crystal structure was determined by X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation. The lattice parameters and tetragonality factors (c/a) of the calcined powders and sintered ceramics were calculated from the XRD patterns. Scanning electron microscopy (SEM) was used to examine the surface morphologies and the cross-section micrographs of the PST25 ceramics. The average particle size and average grain sizes of the powders and ceramics were determined using the mean linear method. Dielectric measurements were performed using an LCR meter (Agilent 4263B), and the measuring frequency was 1 kHz. The ferroelectric transition temperature was determined by using a Differential Scanning Calorimeter (DSC). Densities of the final sintered products were determined by using the Archimedes principle.

Results and Discussion

The XRD patterns of powdered mixtures with various PbO excess contents are shown in Fig. 1(a). The crystal structure of the PST25 was proposed as a tetragonal phase, which could be matched with the JCPDS file number 06-0452 [17]. The pure perovskite structure can be obtained in the powders containing 0 and 1 wt.% excess PbO. On the other hand, when the excess PbO content was greater than 3 wt.% the PbO and PbO_2 phases were present. The second phases occurred because of too much lead for the proper reaction [15, 18]. Figure 1(b) shows the XRD patterns of PST25 sintered ceramics. The impurity phase was not obtained in any ceramic samples. It indicated that the PbO and PbO_2 phase (impurity phase) that had been formed in the PST powders were eliminated from the samples by volatilization during sintering at 1150°C.

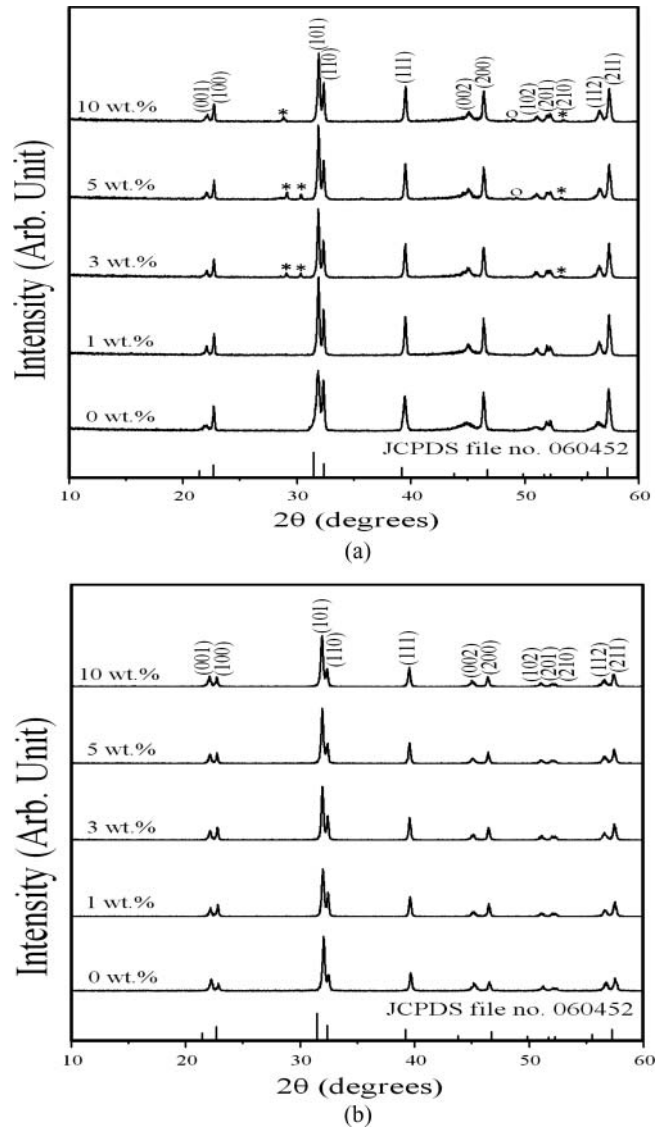


Figure 1. XRD pattern of (a) calcined powders and (b) sintered ceramics made from starting powders contained different amounts of excess PbO: (*) PbO, (o) PbO₂.

The lattice parameters a , c of PST25 calcined powders and sintered ceramics which were calculated from the (001)/(100) and (002)/(200) XRD peaks, are seen in Table 1. The lattice parameter a , c and c/a of the PST25 calcined powders and sintered ceramics tended to decrease with the increase of excess PbO content. These results indicated that the introduction of excess PbO affected the phase formation of PST25 calcined powders and sintered ceramics. The decrease of the tetragonality affected by excess PbO was similar to our previous work on $(\text{Pb}_{0.925}\text{Ba}_{0.075})\text{TiO}_3$ ceramics with excess lead [16].

SEM photomicrographs of PST25 calcined powders with various excess PbO are shown in Fig. 2(a) and (b). The particle size of the samples without excess PbO (0 wt.%)

Table 1
Lattice parameter a , c , c/a ratio, average particle size, average grain size, density and transition temperature of the PST calcined powders and sintered ceramics

Excess PbO (wt%)	Calcined powder			Sintered ceramic				
	Lattice parameter (Å)		Average particle size (μm)	Lattice parameter (Å)		Average grain size (μm)	Density (g/cm^3)	Transition temperature (°C)
	a	c		a	c			
0	3.9159	4.0363	1.0307	3.9032	4.0168	1.18	7.66	311
1	3.9151	4.0252	1.0287	3.9016	4.0143	1.15	7.68	315
3	3.9127	4.0252	1.0281	3.9008	4.0126	1.19	7.56	—
5	3.9111	4.0219	1.0283	3.8992	4.0109	1.21	7.35	—
10	3.9103	4.0210	1.0283	3.8969	4.0084	1.34	7.19	—
								307

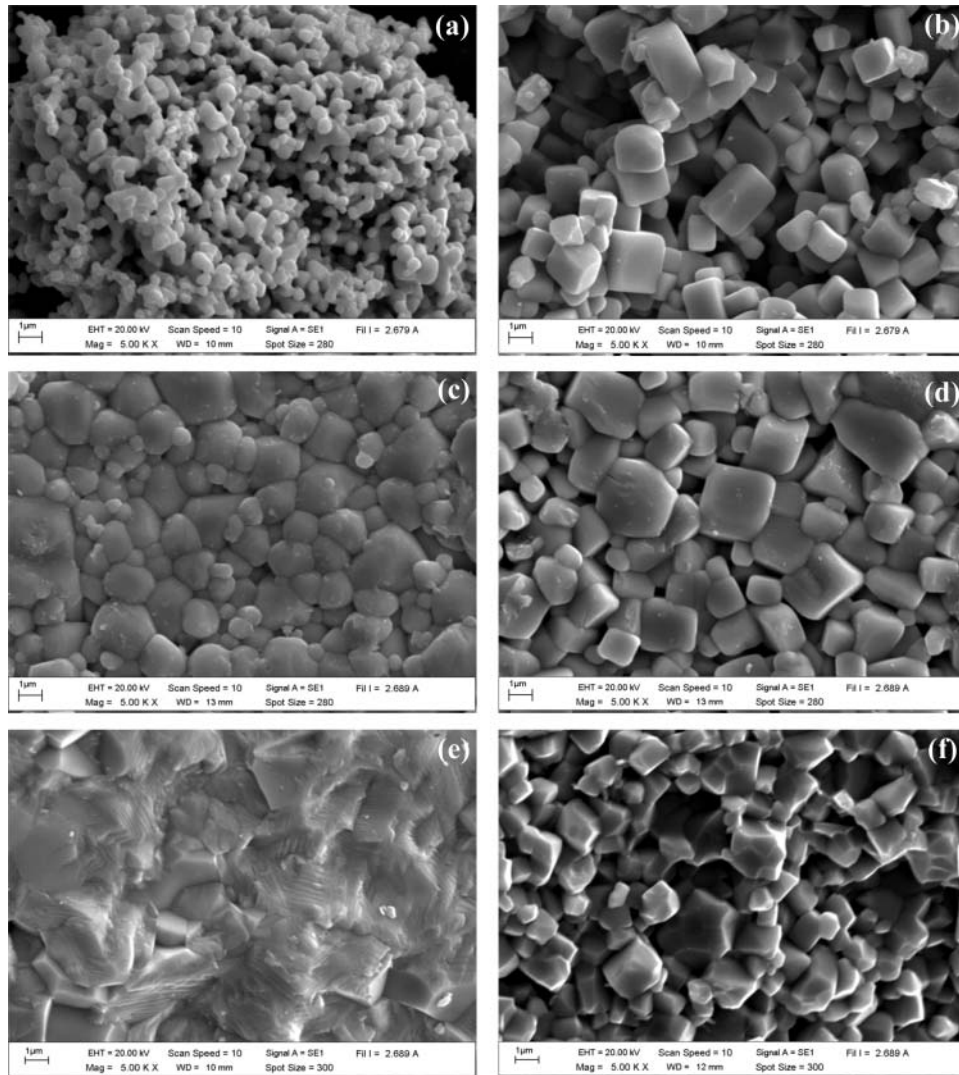


Figure 2. SEM photomicrographs of the calcined powder with excess PbO (a) 0 wt.% (b) 10 wt.%, as sintered surface of the ceramics with excess PbO (c) 0 wt.% (d) 10 wt.%, and fracture surface of the ceramics with excess PbO (e) 0 wt.% (f) 10 wt.%.

exhibited an almost spherical morphology. When the excess PbO increased, the particle size changed from a spherical morphology to nearly cubic shaped and agglomerated. The average particle size increased from $0.62 \mu\text{m}$ to $1.52 \mu\text{m}$ when increasing excess PbO from 0 wt.% to 10 wt.% (Table 1). It is believed that at chosen calcinations temperatures the sintering process starts and, as a consequence, the agglomerates are formed in the calcined PST25 powders [18]. Figures 2(c) and (d) demonstrate SEM photographs of the sintered surfaces of PST25 ceramics with different excess PbO. When the excess PbO increased, the average grain sizes increased from $1.18 \mu\text{m}$ to $1.34 \mu\text{m}$ (Table 1). The addition of excess PbO combined in the grain boundary and formed a grain boundary layer, which hindered the grain growth [15]. Moreover, the porosity decreased with an increasing amount of

PbO until 1 wt.%, then slightly increased in higher excess PbO samples. The cross-section microstructures of the PST25 are displayed in Fig. 2(e) and (f). The samples without excess PbO (0 wt.%) showed transgranular cracking and the fracture was nearly fully intergranular cracking with excess PbO ≥ 3 wt.%. This indicated that in the higher excess PbO samples, residual PbO being present at the grain boundaries caused a change in fracture mode. This is attributed to the presence of PbO at the grain boundaries which makes the grain boundary of the ceramic weaker [19].

The densities of the PST25 ceramics are listed in Table 1. The density slightly increased with an increasing amount of PbO until 1 wt.%, then slightly decreased, for the higher excess PbO. The increase and decrease of density in the PST25 ceramics with excess PbO can be understood by considering the presence of the liquid phase formed due to the low melting point of PbO (850°C). In the presence of excess PbO, the densification of the sample takes place by a rapid rearrangement of the particles surrounded by the liquid PbO. This process becomes more intense if a sufficient liquid phase is present to allow an easy rearrangement of the grains. The proper amount of PbO (≤ 1 wt.%) makes the ceramic dense. However, a large amount of the PbO liquid phase can produce an initial rapid densification but a lower final density as a result of void formation due to the PbO evaporation. As a consequence the porosity of the pellet increases [14, 20]. In summary, the reduction in density for the 3, 5 and 10 wt.% samples is consistent with there being an excessive amount of PbO in these samples.

Figure 3 demonstrates the dielectric constant and dielectric loss (measured at 1 kHz) of PST25 ceramics with various excess PbO content. For the 0 wt.% sample, the maximum value of the dielectric constant ~ 14600 occurred at $\sim 311^\circ\text{C}$ (Table 1) which corresponded to the phase transition from FE to PE. For 1 wt.%, the peak occurred at $\sim 315^\circ\text{C}$ and was broader than 0 wt.%. For 3, 5 and 10 wt.%, no dielectric anomaly corresponding to the FE to PE transition was observed. When the PbO content was over the proper range, a non-uniform distribution was obtained and caused inhomogeneous regions. These regions had different Curie points, and the net effect resulted in the flattened characteristics [21]. Moreover, the dielectric curve showed a higher degree of broadening. This indicated that the phase transition changed from a first-order to a second-order [22]. The dielectric loss increased with the increase of excess PbO. The increase of dielectric loss demonstrated the relationship of the observed mechanism to the increase of space charges due to the movement of free charges in the samples bulk leading to higher conductivity [23].

The DSC thermographs of PST25 on heating cycles are shown in Fig. 4. The endothermic peaks related to the transition from a tetragonal ferroelectric phase to a cubic paraelectric phase. The Curie temperature increased with the increase of excess PbO content and reached a maximum at 3 wt.% and then dropped in value when the excess PbO content was higher than 3 wt.%, as seen in Table 1. The results were similar to the $(\text{Pb}_{0.975}\text{Ba}_{0.025})\text{TiO}_3$ ceramics [18]. It demonstrated that the temperature of the endothermic peaks were increased with excess PbO ≤ 1 wt.% while for ≥ 3 wt.% samples there was a drop in value. The Curie peak was obviously broader with a higher excess PbO from 0 wt.% to 10 wt.%. It also indicated that the phase transition changed from a first-order to a second-order which corresponded to the dielectric measurement. This is the first time it has been shown that the excess of PbO caused by the phase transition changed from a first-order to a second-order. The transition enthalpy decreased from 1.2660 J/g to 0.5301 J/g, when the excess PbO increased from 0 to 10 wt.%. It indicated that the samples with added excess PbO preferred the PE phase. This result was different from excess PbO in PBT ceramics, which preferred the FE phase. The structural reason for this is uncertain at this stage. Furthermore, the endothermic peak of the 3, 5 and 10 wt.% excess PbO samples were observed in the DSC curve, but no anomaly

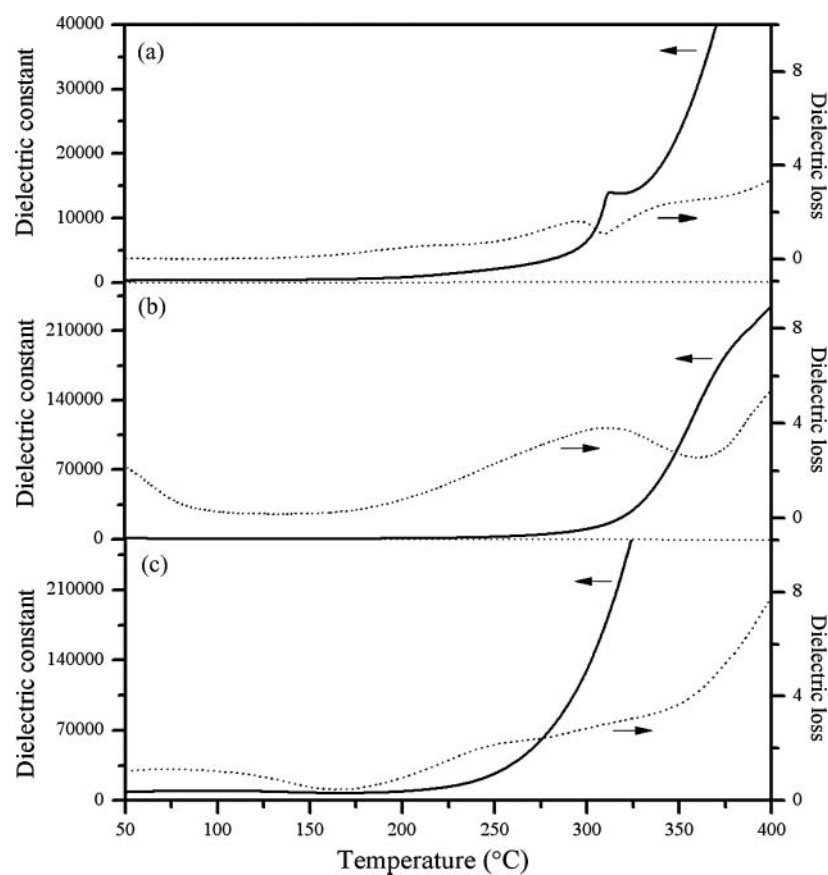


Figure 3. Dielectric constant and dielectric loss versus temperature for PST25 sintered ceramics with different amount of excess PbO: (a) 0 wt.% (b) 3 wt.% (c) 10 wt.%.

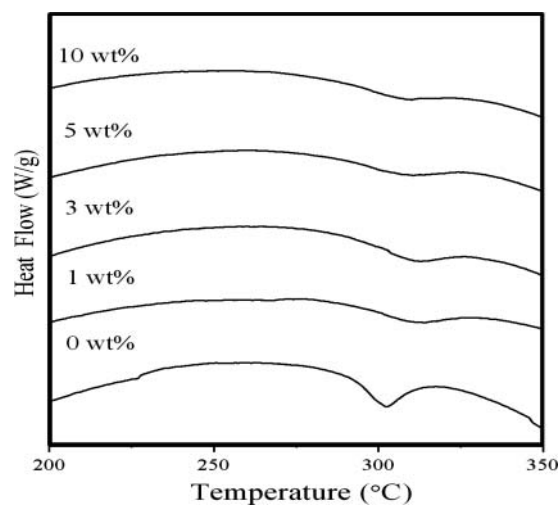


Figure 4. DSC plots showing heating of PBT grounded pellet samples with different amounts of starting excess PbO.

was found in the dielectric constant plot or even in the dielectric loss curve. This suggested that in the detection of a small anomaly of FE-PE in phase transition, the DSC method is more effective than dielectric measurement.

Conclusions

The excess of PbO affected phase formation, microstructure, density, dielectric constant and phase transition. The unreacted PbO and PbO₂ in the calcined powders were employed to compensate lead loss in the sintering process. The tetragonality was decreased by the introduction of excess PbO. The average particle size and average grain size tended to increase with the increase of excess PbO. The densest ceramic was obtained by excess 1 wt.% of PbO. The grain boundary of the ceramics became weaker and the transition changed from first-order to a second-order by additional excess PbO.

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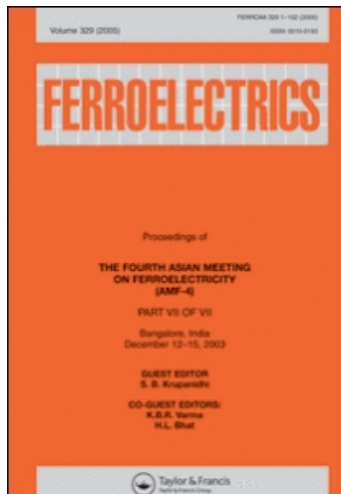
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Ferroelectrics

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The Effects of Firing Temperatures on Phase Formation and Microstructure of $\text{Pb}_{0.975}\text{Sr}_{0.025}\text{TiO}_3$ Ceramics Synthesized via the Combustion Technique

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The Effects of Firing Temperatures on Phase Formation and Microstructure of $\text{Pb}_{0.975}\text{Sr}_{0.025}\text{TiO}_3$ Ceramics Synthesized via the Combustion Technique

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In this work, $\text{Pb}_{0.975}\text{Sr}_{0.025}\text{TiO}_3$ (PST) ceramics were prepared by the combustion technique. Calcination was performed between 700 and 900°C, for 2 h. $(\text{CO}(\text{NH}_2)_2)$ was used as fuel to reduce the reaction temperature. The calcined powders were sintered between 950°C and 1150°C, for 2 h. The samples were characterized using: thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffractometer (XRD), scanning electron microscopy (SEM) and a differential scanning calorimeter (DSC). A single tetragonal perovskite phase was found in the powders calcined above 850°C. The pure perovskite phase was found in all the sintered pellet samples. The c/a ratio decreased with increasing sintering temperatures. The average particle size and the average grain size tended to increase with increasing calcining and sintering temperatures. The maximum density of 98.74% was obtained from the sample sintered at 1100°C. The maximum shrinkage was observed in the sample sintered at 1150°C. The Curie temperature and the enthalpy of the PT ceramics were also investigated by DSC measurement.

Keywords Lead strontium titanate; phase formation; microstructure; combustion technique

Introduction

Lead titanate (PbTiO_3 ; PT) ceramic has a high Curie temperature (T_c) of about 490°C. A high pyroelectric coefficient and spontaneous polarization, make it useful for high frequency and high temperature applications, such as non-volatile memories, infrared sensors and capacitors [1]. It is difficult to prepare pure-phase PT ceramics with high density, because of a high c/a ratio of about 1.06 which gives rise to stresses in these ceramics, so they can be easily broken and are difficult to prepare in a shape and size suitable for device applications [2, 3]. The most widely used approach is the formation of a solid solution by adding rare earth elements and alkaline earth elements. This is a promising technique for producing crack-free high-density materials [4]. For example, adding a small amount of Sr^{2+} , Ba^{2+} and Ca^{2+} to partially substitute Pb^{2+} in the A-site is one of the commonly used methods. Among these, Sr^{2+} has been most widely used because it helps to obtain a higher phase velocity and a high electromechanical coupling coefficient [5].

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There are a lot of processing techniques for preparing lead strontium titanate ceramics. Pe-Jun Wang *et al.* fabricated lead strontium titanate ceramics via the coprecipitation technique [6]. The nitrates of the raw materials were dissolved in a $\text{CH}_3\text{COOH}-\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ system and then coprecipitated by an oxalic acid dehydrate. The precipitate powders were calcined at 700°C for 45 min. After that, Xianran Xing *et al.* prepared $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0 \leq x \leq 1$) by the conventional mixed-oxide method [7]. The samples were calcined at 950°C and sintering temperatures were between 950 and 1250°C . It is well known that ceramics which are synthesized by a solid state reaction method require high temperatures and the resulting powders exhibit many undesirable characteristics: large particle size and wide particle size distribution [8]. Wet chemical synthesis can provide homogenous nanosized oxides of high purity at lower reaction temperatures but they have a high cost for starting materials and they are intricate and complicated [9]. The combustion method is interesting because it helps to decrease the temperature in the preparation and results in a small particle size. The combustion reaction method also has interesting characteristics such as: its simplicity, its relatively low cost, and the fact that it usually results in products with the desired structure and composition [10, 11]. Thus, in this work, $\text{Pb}_{0.975}\text{Sr}_{0.025}\text{TiO}_3$ (PST) ceramics were prepared via the combustion method and the effect of firing temperatures on its phase formation and microstructure were investigated.

Experimental Procedure

$\text{Pb}_{0.975}\text{Sr}_{0.025}\text{TiO}_3$ (PST) was fabricated using an established combustion method. PbO , SrCO_3 and TiO_2 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 120°C for 6 h. Prior to sieving, the powders and urea were mixed in an agate mortar, then calcined between 700 and 900°C for 2 h. The calcined powders were reground by wet ball milling with 2 wt% binder for 24 h. The obtained powders were pressed into the pellets with a diameter of 15 mm prior to sintering between 950 and 1150°C for 2 h. X-ray diffraction (XRD) was performed to examine the phase constitution of the specimens at room temperature. The microstructures of the PST samples were examined using scanning electron microscopy (SEM). The densities of the sintered ceramics were measured by the Archimedes's method and the average grain size was determined by using a mean linear intercept method. Dielectric measurements were performed using an LCR meter (Agilent 4263B), and the measuring frequency was 1 kHz. The phase transition, transformed from tetragonal ferroelectric to cubic paraelectric, was investigated by using a differential scanning calorimeter (DSC).

Results and Discussion

Figure 1 shows the TGA and DTA curves of PST powders and urea prepared by the combustion route. The PST powders demonstrated a three-stage weight loss: the first was in the temperature range of 170 to 235°C , the second from 316 to 450°C and the last began around 675°C . The first weight loss is believed to have been caused by the melting of the urea [12]. It was related to the endothermic peaks in the DTA curves at 170 and 218°C . The second weight loss was caused by the evaporation of water and gas [13]. This was associated with endothermic peaks at 338 , 388 and 414°C . The last curve corresponded to an endothermic peak at 678°C , and a small endothermic peak at 770°C , which may represent the reaction of PbO , SrCO_3 and TiO_2 . Based on the results of DTA and TGA, a

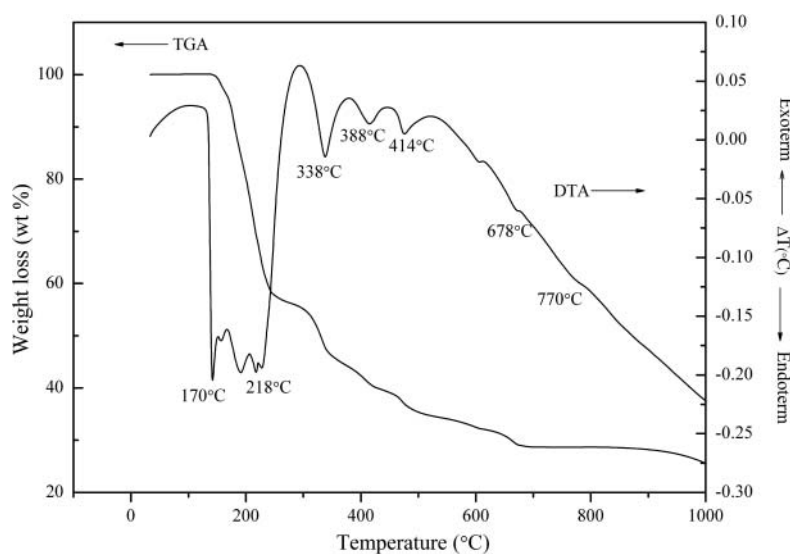


Figure 1. TGA-DTA curves of PST powders and urea.

series of calcinations for the PST powders were carried out from 700 to 900°C for 2 h, at a heating/cooling rate of 5°C/min.

The XRD patterns of the PST powders and ceramics, formed with different calcination and sintering temperatures, are given in Fig. 2. It was found that the PST powders and ceramics indexed in a tetragonal structure which could be matched with JCPDS file number 06-0452. In the samples calcined below 850°C the precursor of the PbO, TiO₂ and SrCO₃ phase were detected (Fig. 2a.). A high purity of the tetragonal perovskite phase was discovered in powders calcined above 850°C. Figure 2b shows a single perovskite tetragonal phase of PST in all sintered samples. The relative percentage in the perovskite and impurity phases was determined by measuring the major XRD peak intensities of the perovskite and impurity phases. The percentage of the perovskite phase is described by the following equation:

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{PbO}} + I_{\text{TiO}_2} + I_{\text{SrCO}_3}} \right) \times 100 \quad (1)$$

This equation is a well-known equation which is widely employed in the preparation of complex perovskite structure materials [14]. Here I_{perov} , I_{PbO} , I_{TiO_2} and I_{SrCO_3} refer to the intensity of the (101) perovskite peak, and the intensities of the highest PbO, TiO₂ and SrCO₃ peaks. The percentage of the perovskite phase of PST compounds are calculated and demonstrated in Fig. 3. The purity of the perovskite phase rose with increasing calcination temperatures and 100% of the perovskite phase was found above 850°C.

The lattice parameter a and c of the PST ceramics increased with increasing sintering temperatures, up to 1000°C. The lattice parameter a and c tended to slightly decrease with higher sintering temperatures (Table 1). The c/a ratio tended to decrease with increased sintering temperatures as seen in Table 1. The changing of the sintering temperature affected the lattice strain, which changed the d spacing and the lattice parameters of the samples [15].

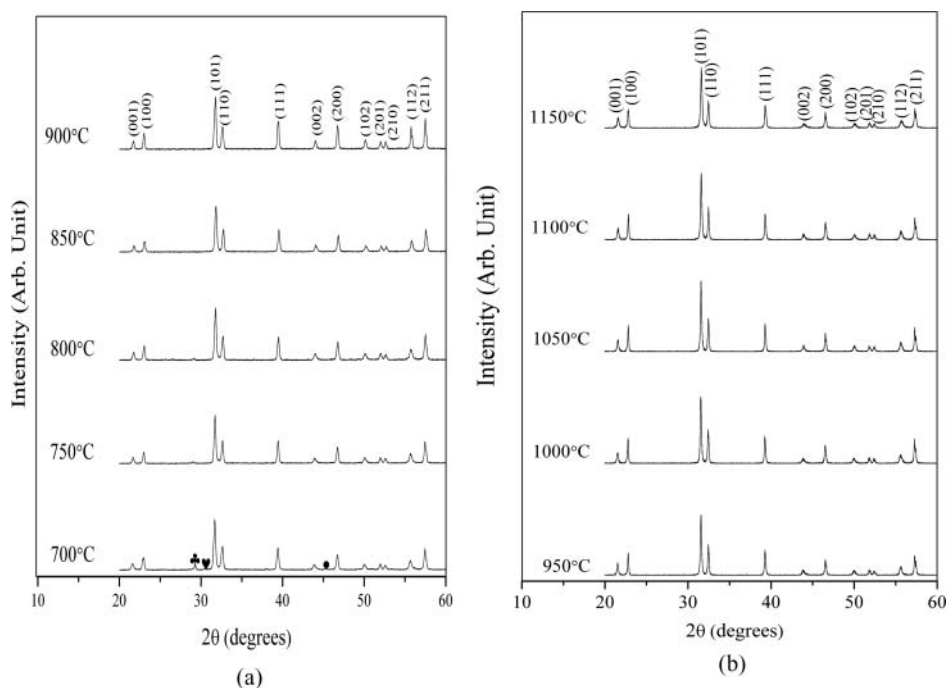


Figure 2. XRD patterns of PST samples with various calcined and sintering temperature: (a) calcined powders; (♣) PbO , (♥) TiO_2 and (●) SrCO_3 and (b) sintered ceramics.

The SEM photomicrographs of PST calcined powders and sintered ceramics are illustrated in Fig. 4. These powders exhibited an almost spherical morphology and have a porous agglomerated form as shown in Fig. 4a and b. The particle size, which is calculated from the cutting lines in SEM, rose from 0.36 to 1.26 μm with the increased calcination temperature

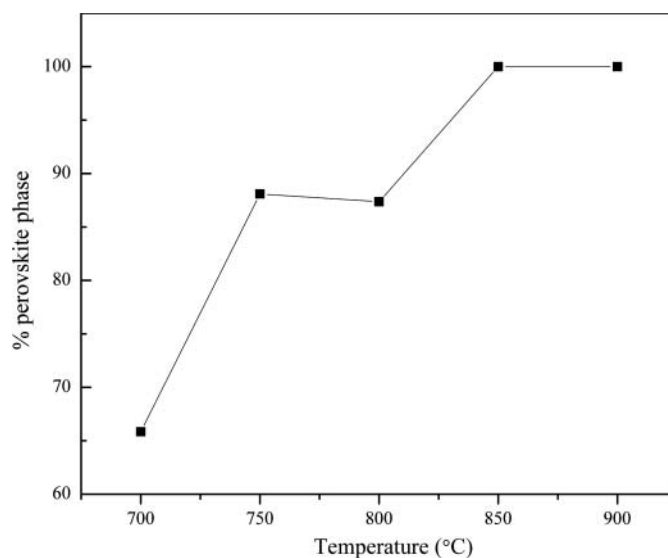


Figure 3. The % perovskite phase of PST powders.

Table 1
Lattice parameter a , c , c/a ratio, average grain size, density, shrinkage, dielectric constant and FE-PE transition of PST ceramics.

Sintered temperature (°C)	Lattice parameter			The c/a ratio	Average grain size (μm)	Density (g/cm^3)	Shrinkage (%)	Dielectric constant at 25°C	FE-PE transition	
	a (Å)	c (Å)							enthalpy (J/g)	Curie Temperature (°C)
950	3.9017	4.1269		1.0577	0.51	7.29	6.8	51	2.321	464.10
1000	3.9037	4.1272		1.0572	0.77	7.67	7.5	253	2.787	464.34
1050	3.9014	4.1231		1.0568	0.87	7.69	9.5	369	3.028	462.56
1100	3.9008	4.1222		1.0568	1.00	7.87	10.7	637	2.817	462.40
1150	3.9020	4.1167		1.0550	1.31	7.83	11.5	491	2.541	459.73

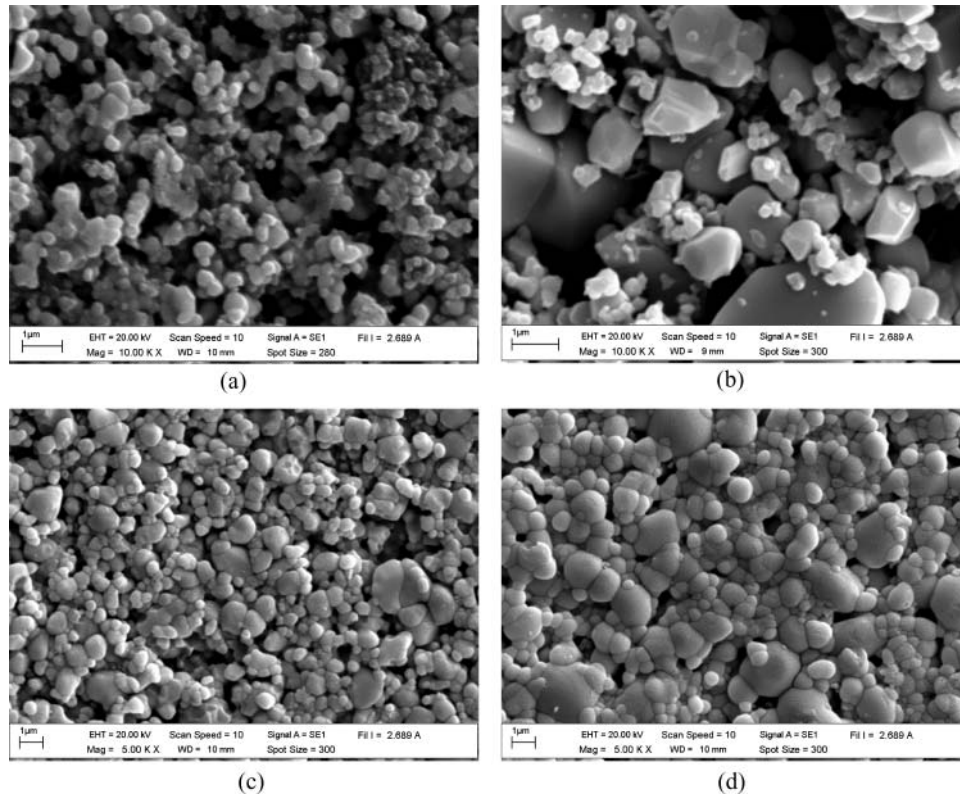


Figure 4. SEM morphology of PST calcined powders and sintered ceramics at (a) 700°C, (b) 900°C, (c) 1000°C and (d) 1150°C.

from 700 to 900°C. Figure 4c and d shows the microstructure and reveals that the grains are nearly spherical in shape with different grain sizes. By using the intercept method, the average grain sizes increased from 0.51 to 1.31 μm (Table 1). The results indicated that the average particle size and average grain size tended to increase with increase calcination and sintering temperatures.

The variation of the measured density and shrinkage of PST ceramics with different sintering temperatures are also shown in Table 1. The density increased with increased sintering temperatures up to 1100°C and decreased with higher sintering temperatures. The shrinkage increased with an increased sintering temperature.

The dielectric constant at room temperature as a function of the sintering temperatures is listed in Table 1. The tendency of dielectric constant values with the sintering temperature is similar to that of the density, while the average grain size also increases monotonically with sintering temperature. This agrees with the report by R. Yimnirun *et al.* [16]. They reported that the maximum dielectric constant of PZT ceramics increased with increasing grain size. The increasing grain size results in a reduction in the volume fraction of grain boundaries, which makes domain reorientation more difficult and severely constrains the domain wall motion. This translates to an increase in the domain wall mobility corresponding to an increase in the dielectric constant [16]. In this study, the increasing dielectric constant in sintering temperatures up to 1100°C can be related to the increasing grain size as shown

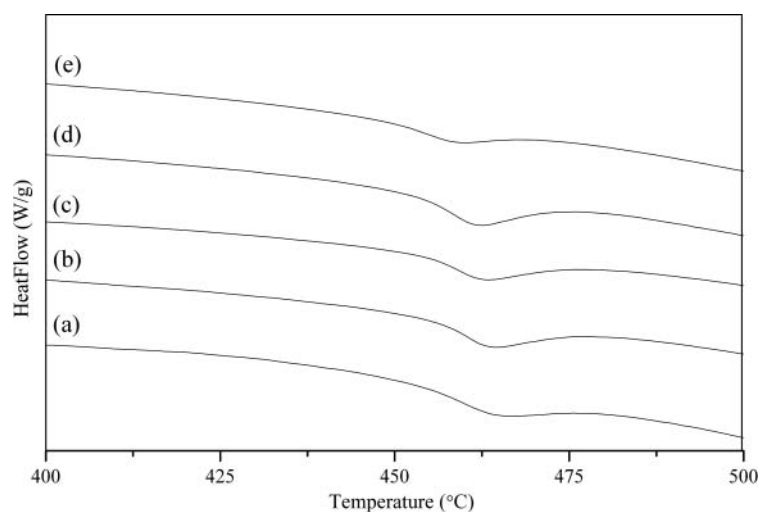


Figure 5. The DSC analysis of the PST ceramics with various the sintering temperature: (a) 950°C, (b) 1000°C, (c) 1050°C, (d) 1100°C and (e) 1150°C.

in Table 1. However, the dielectric constant values of the sintered samples decreased from 637 to 491 as the sintering temperatures increased to 1150°C. This observation may be attributed to a higher PbO deficiency and porosity in PST ceramics at higher sintering temperatures. Thus, the higher sintering temperature can significantly reduce the values of dielectric constant of PST ceramics.

Figure 5 demonstrates the DSC thermograms of sintered samples. The distinct endothermic peak could be attributed to Curie temperature when it transformed from the tetragonal ferroelectric to cubic paraelectric. The Curie temperature slightly increased with an increase of sintering temperatures, up to 1000°C, after that the Curie temperature tended to slightly decrease with higher sintering temperatures (Table 1). The enthalpy increased with an increased sintering temperature, up to 1050°C, afterwards the enthalpy tended to decrease with higher sintering temperatures as seen in Table 1. These results suggested that the sintering temperatures directly affected the Curie temperature and the enthalpy of the PST ceramics.

Conclusions

The densest of the PST ceramics were successfully obtained via the combustion method. A highest purity of the tetragonal perovskite phase was discovered in powders calcined above 850°C. The maximum density was 7.87 g/cm³ or 98.7% obtained from the sample sintered at 1100°C. The *c/a* ratio decreased while average grain size increased with increased sintering temperatures. The average grain size and density can influence dielectric properties. The firing temperatures have directly affected the phase formation, microstructure, density, dielectric constant and FE-PE transition of the PST ceramics.

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Fabrication of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics prepared using the combustion technique

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Abstract

Barium strontium zirconate titanate $((\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3)$; BSZT, $x = 0.25$ and 0.75) ceramics with a highly crystalline structure were successfully synthesized using the combustion technique, in which urea performed an important role. The effect of calcination (1000 – 1300°C) and sintering temperatures (1300 – 1550°C) on the phase formation and microstructure of BSZT ceramics were investigated. The pure perovskite phase of BSZT ($x = 0.25$ and 0.75) powders with a uniform cubic morphology were detected at the calcination temperature of 1300°C . At the same calcination and sintering temperature, the lattice parameter a of BSZT powder and ceramics with $x = 0.75$ is higher than $x = 0.25$. The microstructure of BSZT powders exhibited an almost-spherical morphology and had a porous agglomerated form. The average particle size and the average grain size of all ceramics increased with the increase of calcination and sintering temperatures, but decreased when the content of x increased. The maximum densities of $x = 0.25$ and 0.75 ceramics were around 5.85 and 5.62 g cm^{-3} obtained from the samples sintered at 1500 and 1450°C , respectively.

1. Introduction

Solid solutions of barium titanate and strontium zirconate; $(1-x)\text{BaTiO}_3$ – $x\text{SrZrO}_3$ exist in a single phase for wide range of compositions. The paraelectric $(1-x)\text{BaTiO}_3$ – $x\text{SrZrO}_3$; $x \geq 0.2$ ceramics are chemically more stable, and have a lower transition temperature (T_c) and a high dielectric constant [1]. $(1-x)\text{BaTiO}_3$ – $x\text{SrZrO}_3$ compounds have been applied in microwave dielectric resonators, which are miniature resonating devices used in microwave integrated circuits [2]. The tunability and figure of merit of $(\text{Ba}_{0.75}\text{Sr}_{0.25})(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ thin films are 53% and 38, respectively, and are promising candidates for microwave tunable devices [1, 3]. A literature survey revealed that the sol–gel technique has been used to prepare $(1-x)\text{BaTiO}_3$ – $x\text{SrZrO}_3$ powders [4–6]. It is well known that this process of sample preparation is complex and expensive [7]. Our previous work prepared and characterized $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics by the solid state reaction method [8, 9]. The pure phase was obtained at a

calcination temperature over 1350°C and a maximum density of around 5.42 – 5.64 g cm^{-3} was found from the sample sintered at over 1500°C . Recently, the combustion technique has become an attractive technique for synthesizing different oxides, such as BaTiO_3 [10], BaZrO_3 [11], SrZrO_3 [12], CaZrO_3 [13]. This technique involves a self-sustained reaction between the reactive materials and the fuel (e.g. urea), which provides a liquid medium at the start of the reaction. In a liquid environment, the reaction can take place more easily because the diffusion coefficient is higher than in the solid medium. Furthermore, with the high surface energy and driving force of the combustion technique, fine, highly crystalline powders with the desired composition were also obtained [11, 14].

However, a detailed study of the synthesis and characterization of $((\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3)$; BSZT ceramics via the combustion technique has not been reported in the literature. So, in this work, BSZT ($x = 0.25$ and 0.75) ceramics were prepared via the combustion technique. The effects of calcination, sintering temperatures and the replacement of ions at the A and B sites on the phase formation and microstructure of BSZT ceramics were also investigated.

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2. Experimental details

Barium strontium zirconate titanate ($(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$; BSZT, $x = 0.25$ and 0.75) powders were synthesized by the combustion technique. The mixtures, in the required stoichiometric ratio of BaCO_3 (99%), SrCO_3 (99%), ZrO_2 (99%) and TiO_2 (99%), were ground by a ball milling procedure (zirconia milling media under ethanol for 24 h). They were then dried at 120°C for 4 h. The mixture of raw materials and the fuel, urea in the ratio of 1:2 by weight, was mixed well before the calcination step. The reaction of the uncalcined powders with the urea taking place during heat treatment was investigated by thermogravimetric and differential thermal analysis (TGA–DTA) using a heating rate of $10^\circ\text{C min}^{-1}$, in air, from room temperature up to 1275°C . Afterwards, the mixed powders were calcined in temperatures ranging from 1000 to 1300°C , with a dwell time of 4 h and a heating/cooling rate of 5°C min^{-1} . The calcined powders were then pressed into discs with a diameter of 15 mm at a pressure of 80 MPa. The pellets were sintered from 1300 to 1550°C for 2 h and cooled in a furnace. X-ray diffraction (XRD) was employed to identify the phase formed and the optimum temperature for the formation of BSZT powders and ceramics. The morphological features of the product were imaged using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The density of the sintered ceramics was measured by the Archimedes method. The average particle size and the average grain size were determined by using the mean linear intercept method. The raw data were obtained by measuring the particle and grain sizes over 300 particles and grains.

3. Results and discussion

The simultaneous TGA–DTA analyses of the powders mixed in stoichiometric proportions of $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$; BSZT, $x = 0.25$ and urea are exhibited in figure 1(a). In the temperature range from room temperature to $\sim 250^\circ\text{C}$, the first weight loss occurred around 130 – 280°C , and demonstrated endothermic peaks at 142 and 201°C in the DTA curve. These observations can be related to the melting of urea, which normally occurs at about 135°C [14]. The second weight loss occurred between 280 and 420°C , and is related to the endothermic peak at 398°C in the DTA curve. These observations may be correlated with the rapid vaporization of water and gas caused by the decomposition of ammonia [18]. The third weight loss occurred between 450 and 600°C , and corresponds to the endothermic peak at 494°C . This step may be related to the vaporization of water and gas [18], but the rate of vaporization was lower than in the second step. The combustion reaction process occurred in these three steps. The molten urea and the decomposition of the ammonia provided a liquid environment in which the diffusion coefficient was higher than in the solid medium. This caused the raw materials to have a more uniform distribution. Furthermore, the energy obtained from the combustion of the urea and the oxidation–reduction reaction between the ammonia and NO was also released. The combustion energy reduced the particle size

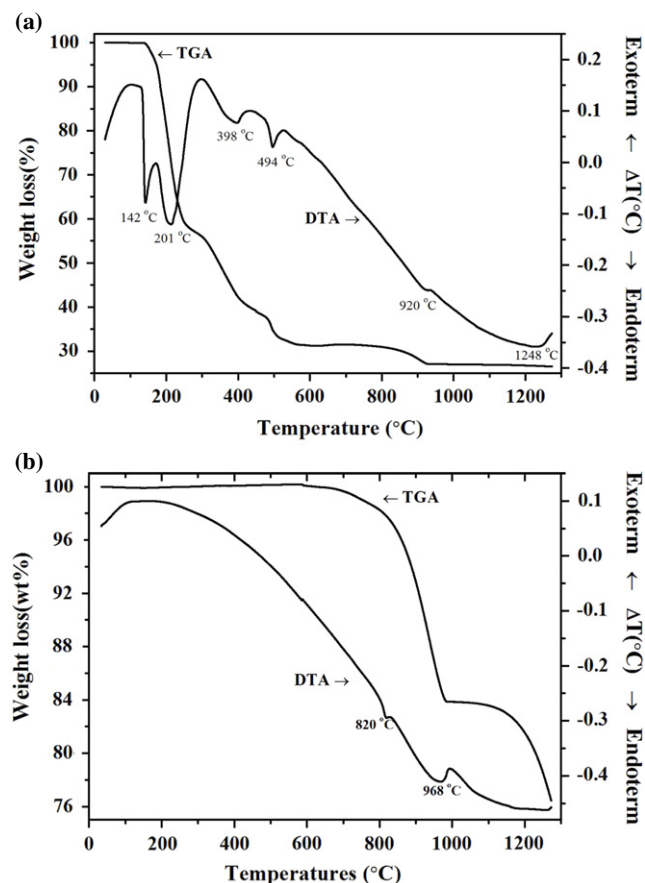


Figure 1. TGA–DTA curves for the mixture ($x = 0.25$) of (a) the raw materials and urea, and (b) only the raw materials.

of the powders. This chemical reaction takes place easily and accelerates the reaction in the next step. The fourth weight loss occurred between 600 and 925°C , which correlates with small endothermic peaks at 920°C . These observations showed the chemical reactions of the raw materials. The last weight loss occurred at higher than 930°C . It was almost stable but an endothermic peak occurred at 1248°C , indicating that the solid state reaction of the raw materials continued. These results were used to identify the range of different calcination temperatures between 1000 and 1300°C for XRD investigation.

The simultaneous TGA–DTA analyses of composite BSZT powders of $x = 0.25$ without urea are shown in figure 1(b). The TGA curve showed two distinct weight losses. The first weight loss started at around 595°C , which relates to a small endothermic peak in the DTA pattern at around 820°C . The second weight loss occurred above 960°C , which correlates with a small endothermic peak around 968°C . These observations demonstrated the chemical reaction between BaCO_3 , SrCO_3 , ZrO_2 and TiO_2 . Moreover, it was seen that the chemical reaction still continued at temperatures over 1300°C , whereas the complete chemical reaction using the combustion method should not be higher than 1300°C .

The XRD patterns of BSZT powders with $x = 0.25$ at different calcination temperatures are shown in figure 2(a). The diffraction lines were indexed on the basis of a cubic structure

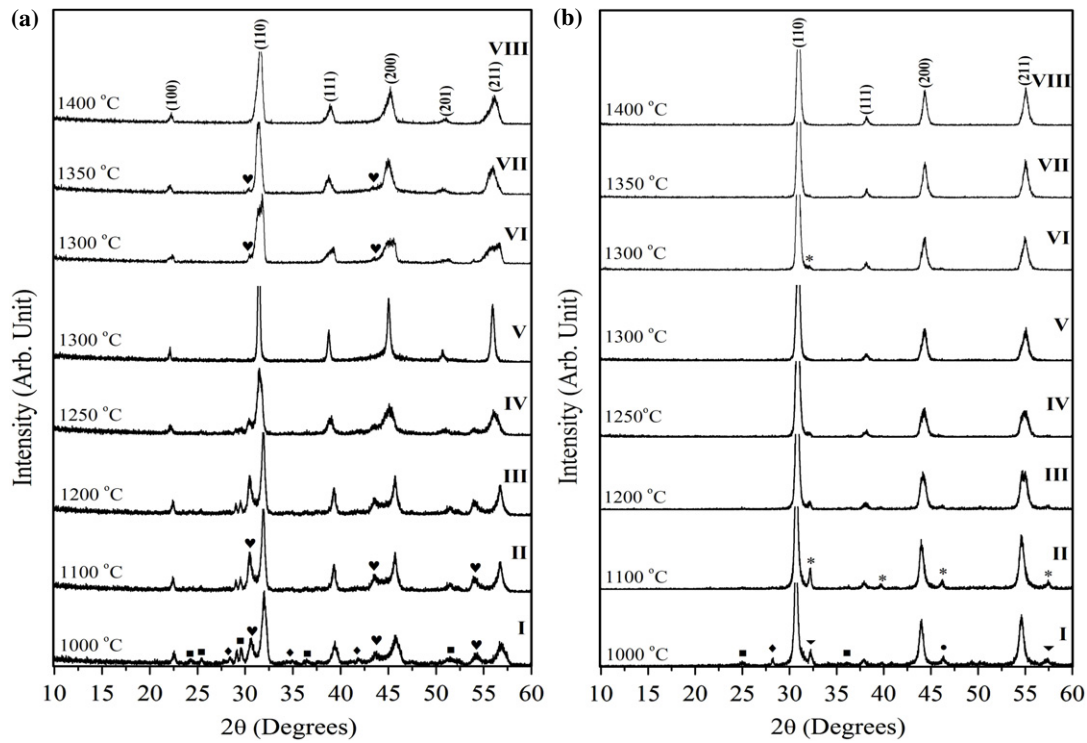


Figure 2. XRD patterns of BSZT powders with (a) $x = 0.25$ and (b) $x = 0.75$, I–V mixed urea and VI–VIII without urea, which were calcined at various temperatures for 4 h: (♥) BaZrO₃; (♦) BaO; (●) BaTiO₃; (■) TiO₂; (▼) ZrO₂; (*) SrTiO₃.

Table 1. The percentage of perovskite phase, lattice parameter a and average particle size of BSZT powders.

Calcined temperature	$x = 0.25$			$x = 0.75$		
	Percentage perovskite phase (%)	Lattice parameter a (Å)	Average particle size (nm)	Percentage perovskite phase (%)	Lattice parameter a (Å)	Average particle size (nm)
1000	65.7	3.9636	210 ± 32	66.5	4.0811	130 ± 31
1100	65.5	3.9652	220 ± 37	72.9	4.0751	150 ± 43
1200	68.2	3.9693	300 ± 33	85.0	4.0725	160 ± 34
1250	79.8	4.0202	320 ± 54	95.3	4.0699	180 ± 29
1300	100	4.0236	370 ± 29	100	4.0682	220 ± 32

matched with JCPDS file number 31-0174. Impurity phases of BaO, BaZrO₃ and TiO₂ were discovered at calcination temperatures below 1300 °C (figure 2(a) I–IV). The pure cubic perovskite phase was found at a calcined temperature of 1300 °C, as shown in figure 2(a) V. The relative amounts of the perovskite phase were determined by measuring the major XRD peak intensities of the perovskite phase. The percentage of the perovskite phase can be calculated by the following equation:

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{BaO}} + I_{\text{BaZrO}_3} + I_{\text{TiO}_2}} \right) \times 100. \quad (1)$$

This equation is well-known and widely employed in the preparation of complex perovskite structure materials [8, 9, 11]. Here I_{perov} , I_{BaO} , I_{BaZrO_3} and I_{TiO_2} refer to the intensity of the (101) perovskite peak and the intensities of the highest BaO, BaZrO₃ and TiO₂ peaks, respectively. The percentage of perovskite phase of BSZT powders calcined for 4 h

at temperatures ranging from 1000 to 1300 °C is shown in table 1. The increase of phase purity with increasing calcination temperatures is evident.

Figure 2(b) illustrates the diffraction line of BSZT calcined powders with $x = 0.75$, which can be indexed on the basis of a cubic structure matched with JCPDS file number 03-0632 and corresponds to previous works [8, 9]. Impurity phases of BaO, BaTiO₃, SrTiO₃, ZrO₂ and TiO₂ were discovered at calcination temperatures below 1300 °C (figure 2(b) I–IV). The pure cubic perovskite phase was found at a calcined temperature of 1300 °C, as illustrated in figure 2(b) V. The percentage of the perovskite phase increased when the calcined temperatures increased, as shown in table 1.

In the case without urea [8, 9], the impurity phases of BaZrO₃ and SrTiO₃ were still detected at calcination temperatures of 1350 and 1300 °C for $x = 0.25$ and 0.75, as shown in figure 2(a) VI–VII and figure 2(b) VI, respectively. The pure cubic perovskite phase of BSZT powders of $x = 0.25$ and 0.75 was detected at calcination temperatures of 1400 and

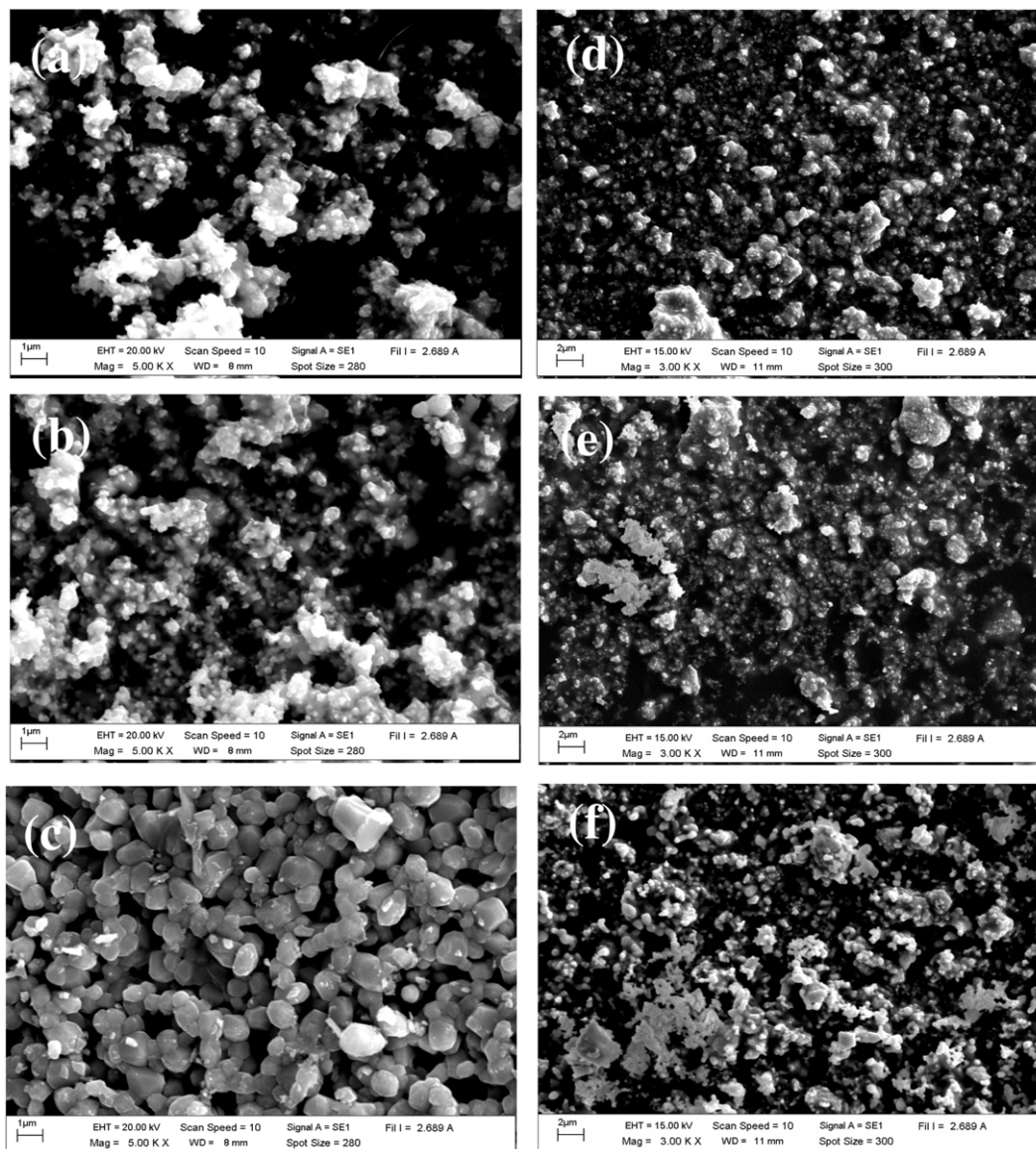


Figure 3. SEM photographs of BSZT powders with $x = 0.25$ calcined for 4 h at (a) 1000 °C, (b) 1200 °C and (c) 1300 °C, and $x = 0.75$ calcined for 4 h at (d) 1000 °C, (e) 1200 °C and (f) 1300 °C.

1350 °C, as shown in figure 2(a) VIII and figure 2(b) VII. The optimum calcination temperature of the combustion technique was lower than that of the solid state reaction method [8, 9] by around 50–100 °C. This is because the interior reactant of the combustion technique appears at an instantaneous high local temperature, which is around 1500 °C [14], with a smaller particle size and a more uniform distribution. These results corresponded to the TGA–DTA investigation. At the same calcination temperature, the lattice parameter a of the calcined powders with $x = 0.75$ in value was higher than the lattice parameter a of $x = 0.25$. The changing of firing temperatures and the ions in the A and B sites affected the lattice strain, which determines the change in the d spacing and the lattice parameters of the samples [15]. This indicated that the calcination temperatures and increasing x content affected the crystal structure and the phase formation.

Figures 3(a)–(f) show SEM photographs of BSZT powders with $x = 0.25$ and 0.75 that were calcined at 1000 and 1300 °C for 4 h. These powders exhibited an almost identical spherical morphology with a variation in size and had a porous agglomerated form. The average particle size of the BSZT powders increased as the calcination temperatures increased. The variation of x content also influences the particle size. The average particle size for $x = 0.25$ is larger than for $x = 0.75$ at the same calcination temperature, as shown in table 1.

Figure 4 shows a typical TEM micrograph of the BSZT powder with $x = 0.75$. The average agglomerate size of the as-calcined powders was assessed as around 230 nm when observed by TEM in a low magnification image, as shown in figure 4(a). The details of the aggregated particles are seen in the high magnification image in figure 4(b). It can be seen that the powder particles have a similar spherical shape and a porous agglomerated form. The size of the fine primary

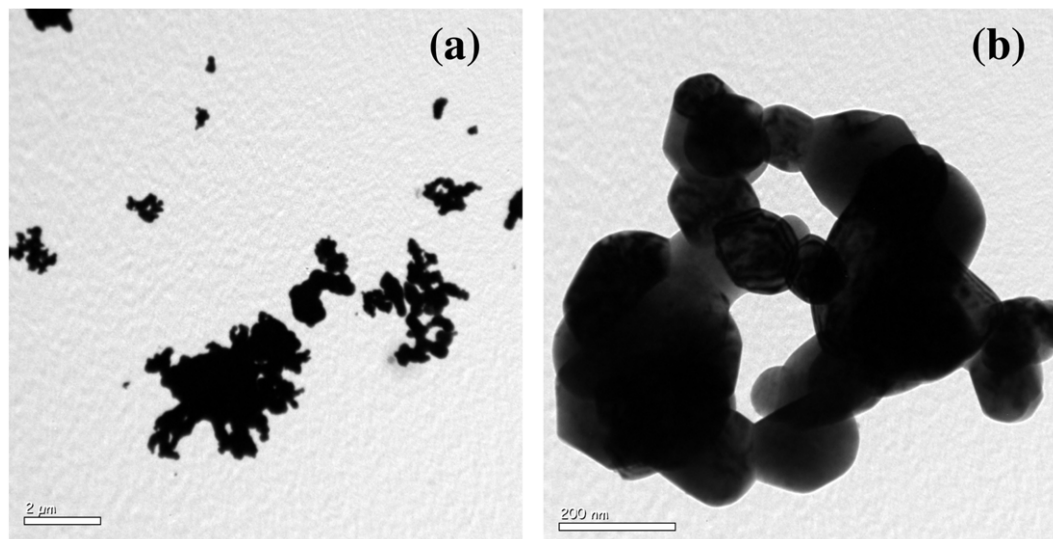


Figure 4. TEM micrograph of BSZT powder with $x = 0.75$ calcined at 1300°C ; (a) low magnification image and (b) high magnification image.

particles is in the range of 89–167 nm. This result showed little difference in its values when compared with the particle sizes from the SEM image. It demonstrates that the TEM results are related to the particle size seen in the SEM results.

Calcined powders of all compositions obtained at 1300°C were pressed into pellets and sintered from 1300 to 1550°C for 2 h. Figure 5 shows the XRD patterns of BSZT sintered ceramics with $x = 0.25$ and 0.75 . The BSZT ceramics with $x = 0.25$ were identified as a single phase of a perovskite structure that has a cubic symmetry in samples sintered below 1550°C . The peaks of BaTiO_3 and SrTiO_3 were detected at 1550°C , which may be due to the vaporization of Zr^{4+} at high temperatures. The BSZT ceramics with $x = 0.75$ were identified as a single phase of a perovskite cubic structure in the samples sintered below 1500°C . The peak of SrTiO_3 was detected at over 1500°C , which may be due to the vaporization of Ba^{2+} and Zr^{4+} at high temperatures.

The lattice parameter a , as a function of sintering temperatures, is shown in table 2. At the same sintering condition, the lattice parameter a of BSZT ceramics was higher for $x = 0.75$ than for $x = 0.25$. The increase in the lattice parameter a may be caused by the change of lattice strain, which was similar to the calcined powders. The reflection peaks were sharper with higher sintering temperatures, which was indicated by the larger crystallization when the sintering temperatures increased.

SEM photographs of the BSZT surface of the sintered ceramics with $x = 0.25$ and 0.75 are shown in figure 6. It was obvious that the porosity decreased, while the average grain sizes increased from 0.91 to $10.57\ \mu\text{m}$ for $x = 0.25$, and from 0.81 to $8.67\ \mu\text{m}$ for $x = 0.75$ with an increase in sintering temperature from 1300 to 1550°C , as shown in table 2.

The percentage shrinkage of the pellet samples increased with the increase of sintering temperatures, as shown in table 2. The density measured with varying x contents and sintering temperature is shown in table 2. The density increased at first with sintering temperature, reaching peaks at 1500 and

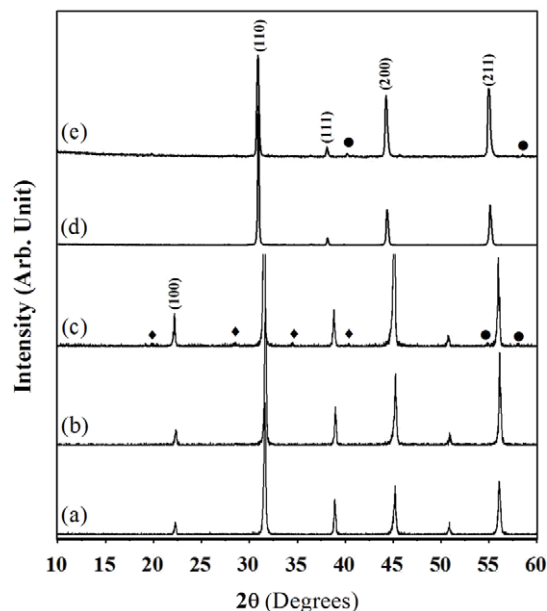


Figure 5. XRD patterns of BSZT ceramics with $x = 0.25$ sintered for 2 h at (a) 1350°C , (b) 1450°C , (c) 1550°C , and $x = 0.75$ sintered for 2 h at (d) 1450°C , (e) 1500°C : (◆) BaTiO_3 ; (●) SrTiO_3 .

1450°C for $x = 0.25$ and 0.75 respectively, then decreased for sintering temperatures beyond these values, as shown in table 2. It was observed that the density decreased when the firing temperature was higher than an optimal temperature for the sintering process. The grain growth correlated with the densification mechanisms during treatment, particularly during the final stage of sintering. The expansion of trapped gases in the pores assembled and grew because of grain growth [16, 17]. Using the optimal heat sintering treatment, 5.85 and $5.62\ \text{g cm}^{-3}$, for $x = 0.25$ and 0.75 respectively, was obtained as the most dense BSZT samples. Although the maximum density of samples prepared by the combustion technique was similar to that of the samples synthesized by

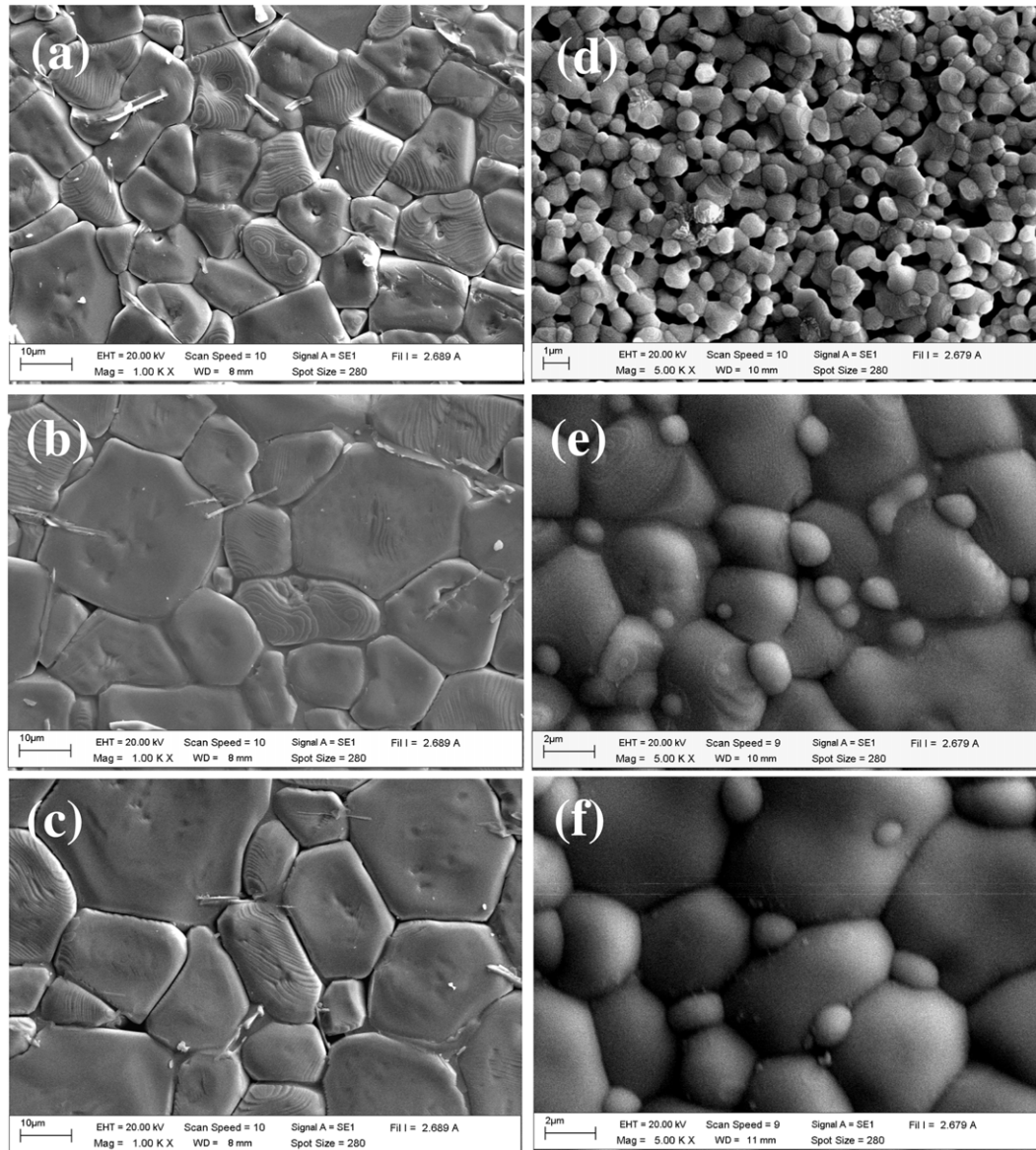


Figure 6. SEM photographs of the pellet surface with $x = 0.25$ sintered for 2 h at (a) 1400 °C, (b) 1450 °C and (c) 1500 °C, and $x = 0.75$ sintered for 2 h at (d) 1400 °C, (e) 1500 °C and (f) 1550 °C.

Table 2. The lattice parameter a , density, shrinkage and average grain size of BSZT ceramics.

Sintering temperature	$x = 0.25$				$x = 0.75$			
	Lattice parameter a (Å)	Average grain size (μm)	Density (g cm^{-3})	Shrinkage (%)	Lattice parameter a (Å)	Average grain size (μm)	Density (g cm^{-3})	Shrinkage (%)
1300	4.0010	0.9 ± 0.10	5.01	14.0	4.0886	0.5 ± 0.05	5.32	3.8
1350	4.0076	1.2 ± 0.32	5.25	14.1	4.0781	0.8 ± 0.07	5.39	6.0
1400	4.0090	2.2 ± 0.43	5.36	14.2	4.0763	1.1 ± 0.12	5.48	10.0
1450	4.0150	5.6 ± 0.71	5.38	15.0	4.0711	2.6 ± 0.20	5.62	16.6
1500	4.0167	8.7 ± 1.30	5.85	15.5	4.0677	5.8 ± 0.35	5.58	17.3
1550	4.0193	10.6 ± 1.34	5.61	16.5	4.0590	8.6 ± 0.68	5.56	18.6

the solid state reaction method, the combustion technique used lower calcination and sintering temperatures [8, 9]. This demonstrates the efficiency of the combustion technique in the preparation of highly pure and dense BSZT ceramics.

4. Conclusions

BSZT powders can be obtained by the combustion technique. The pure cubic perovskite phase was obtained with a

calcination temperature of 1300 °C for both powders. The resulting BSZT powders became more agglomerated as the calcination temperature increased. The maximum densities of 5.85 and 5.62 g cm⁻³ were achieved for ceramics sintered at 1500 and 1450 °C for 2 h. The molten urea and combustion of urea plays an important role in the complete process. The calcination and sintering temperatures, and the replacement of ions at the A and B sites have a strong influence on the crystal structure, lattice parameter and homogeneity of the calcined powders and the sintered ceramics.

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