

Synthesis and microstructure of SrTiO₃ and BaTiO₃ ceramics by a reaction-sintering process

Yi-Cheng Liou · Chi-Ting Wu · Tzu-Chin Chung

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Abstract Strontium titanate and barium titanate ceramics prepared by a reaction-sintering process were investigated. The mixture of raw materials of stoichiometric SrTiO₃ and BaTiO₃ was pressed and sintered into ceramics without any calcination stage involved. A density 4.99 g/cm³ (97.5% of the theoretic value) was found in SrTiO₃ after 6 h sintering at 1,370 °C. Grains less than 1.5 μm were formed at 1,300–1,330 °C and became 2.2–3.3 μm at 1,350–1,370 °C SrTiO₃. A density 5.89 g/cm³ (97.9% of the theoretic value) was found in BaTiO₃ after 6 h sintering at 1,400 °C. Merged grains were observed in BaTiO₃ and were less than 10 μm after sintered at 1,400 °C.

Introduction

Barium titanate (BaTiO₃; BT) and strontium titanate (SrTiO₃; ST) perovskite ceramics are important electric materials and have been widely investigated. BT is extensively used in multilayer ceramic capacitors (MLCCs) [1, 2], positive temperature coefficient (PTC) thermistors [3] and piezoelectric transducers. It is a typical ferroelectric material with Curie temperature around 130 °C. ST is used as capacitors and varistors [4]. As Sr²⁺ ions are partially substituted at Ba²⁺ ions in BT, the Curie temperature could be adjusted linearly in Ba_xSr_{1-x}TiO₃ (BST) system for

$x < 0.75$ [5]. BST thin films are promising materials for high-density dynamic random-access memories (DRAMs) [6, 7]. BST ceramics are considered good candidates for the application in phased array antenna [8] as well as in capacitors, sensors and PTC thermistors [9–11]. The traditional process of synthesizing BT is by a solid-state reaction based on calcining the mixed oxide or carbonate powders. However, the calcined powders usually consist of chemically inhomogeneous particles with large grain sizes. This makes it hard to be used as raw material for advanced electronic components. Therefore, other wet chemical processes including oxalate, sol-gel, coprecipitation and hydrothermal synthesis have been reported [12–14]. A novel mechanochemical processing route has been used to produce BT powder [15, 16]. In this mechanical technique, the powder of reactants are homogenized and activated in high energy vibromill. Several ceramic materials such as PbTiO₃ (PT), Pb(Zr,Ti)O₃ (PZT) and Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) were also prepared by this process [17–19].

Reaction-sintering process is a simple and effective route to synthesize ceramics. The calcination step is bypassed and the mixture of the raw materials is sintered directly. Kong and Ma proposed PZT ceramics prepared by sintering the oxide mixture directly [20]. Almost at the same time, Liou et al. proposed reaction-sintering process in preparing PMN, PMN-PT and Pb(Fe_{0.5}Nb_{0.5})O₃ (PFN) ceramics [21–25]. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without having to go through the calcination step or the high-energy milling. PMN ceramics with a density of 8.09 g/cm³ and dielectric constant 19,900 (1 kHz) are obtained. This reaction-sintering process had also been used to produce other

Y.-C. Liou (✉) · C.-T. Wu · T.-C. Chung
Department of Electronic Engineering, Kun-Shan
University, Tainan Hsien, Taiwan, ROC
e-mail: ycliou@mail.ksu.edu.tw

complex perovskite relaxor ceramics including BPZN, PNN, PMN-PZN, PMN-PFN, PFN-PFW, PNN-PT and PZN-PFN-PFW successfully [26–31]. In the latest studies, we also prepared pure phased BaTi₄O₉ and NiNb₂O₆ microwave ceramics by this process successfully [32, 33]. In the present investigation, synthesis and microstructure of SrTiO₃ and BaTiO₃ ceramics by a reaction-sintering process was reported.

Experimental procedure

All samples in this study were prepared from reagent-grade oxides: BaCO₃ (99.9%), SrCO₃ (99%), and TiO₂

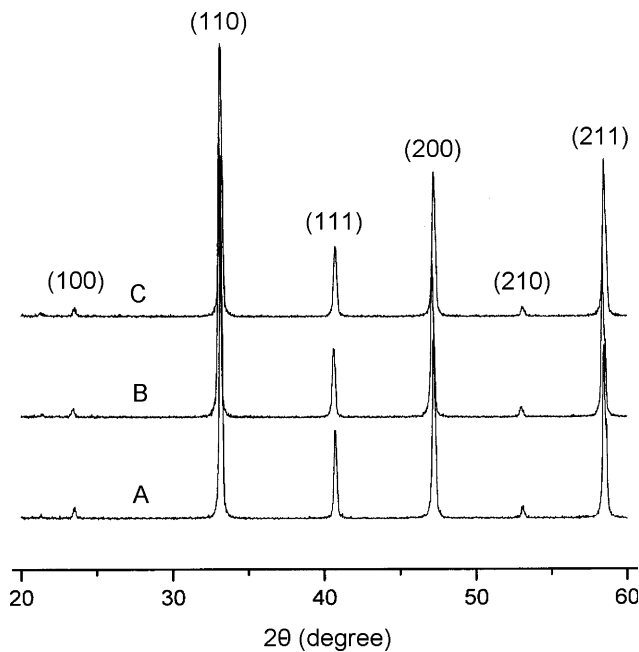


Fig. 1 XRD patterns of ST ceramics sintered at 1,370 °C for (a) 2 h, (b) 4 h and (c) 6 h

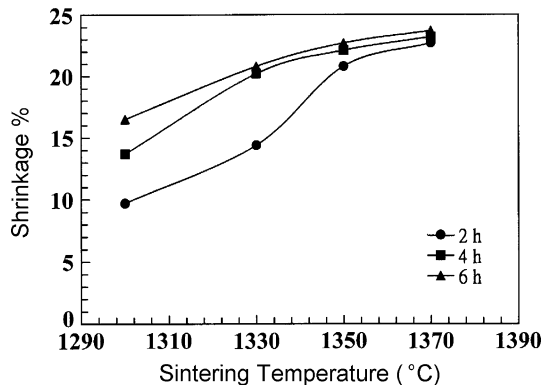


Fig. 2 Shrinkage percentage of ST ceramics sintered at various temperatures and soak time

(99.9%). Appropriate amounts of raw materials for stoichiometric SrTiO₃ and BaTiO₃ were milled in acetone with zirconia balls for 12 h. After dried and pulverized the slurry, the powder was then pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were heated at a rate 10 °C/min and sintered in covered alumina crucible at temperatures ranging from 1,300 °C to 1,400 °C for 2–6 h in air.

The sintered pellets were analyzed by X-ray diffraction (XRD) to check the reflections of the phases. Microstructures were analyzed by scanning electron microscopy (SEM). After polishing, the dimensions were measured before silver electrodes were formed on the pellets. The density of sintered pellets was measured by the Archimedes’s method. The dielectric constant was measured by Agilent 4263B LCR meter.

Results and discussions

SrTiO₃

All ST pellets are found of pure perovskite phase after sintered at 1,300–1,370 °C for 2–6 h. The XRD patterns of ST ceramics sintered at 1,370 °C for 2–6 h are

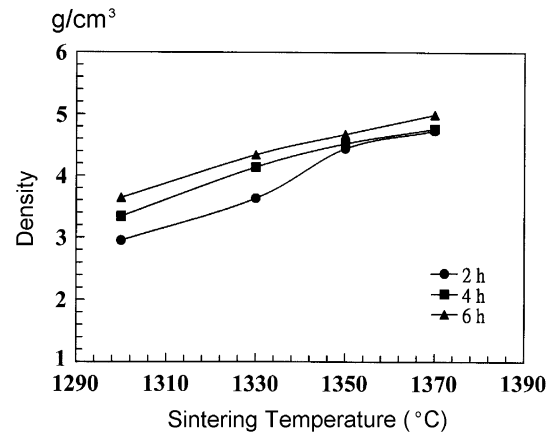
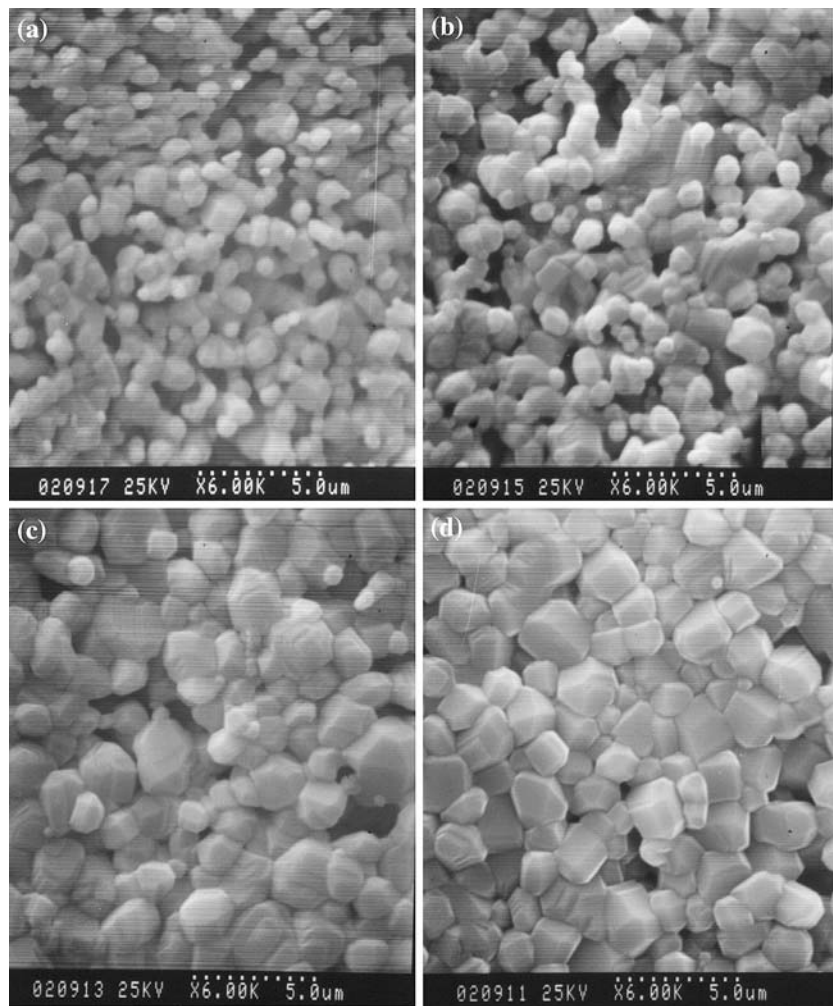


Fig. 3 Density of ST ceramics sintered at various temperatures and soak time

Table 1 The mean grain size of ST ceramics sintered at various temperatures for 2–6 h soak time (in μm)

Sintering temperature	2 h	4 h	6 h
1,300 °C	<1	1.0	1.2
1,330 °C	<1	1.2	1.4
1,350 °C	2.2	2.4	2.6
1,370 °C	2.5	2.7	3.3

Fig. 4 SEM photographs of as-fired ST ceramics sintered at (a) 1,300 °C, (b) 1,330 °C, (c) 1,350 °C and (d) 1,370 °C for 4 h

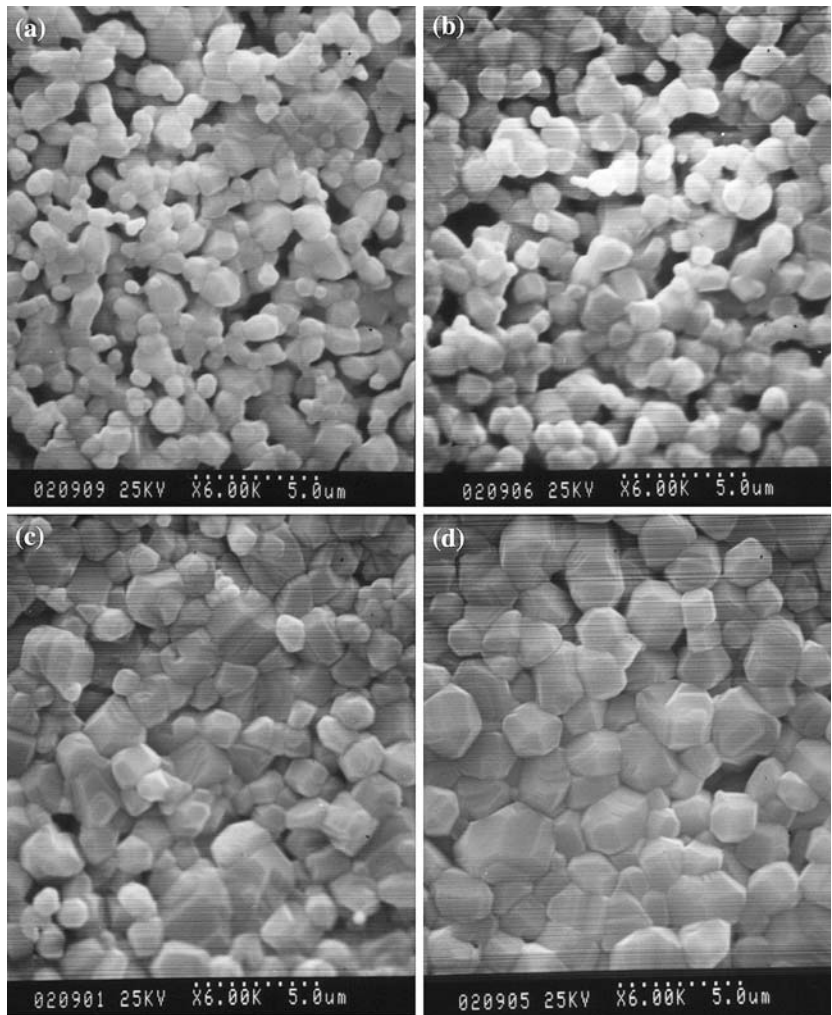


shown in Fig. 1. Perovskite ST ceramics were obtained by the reaction-sintering process with the calcination bypassed. This indicates that the reaction-sintering process is a simple and effective method to produce ST ceramics. The shrinkage percentages of sintered ST pellets are illustrated in Fig. 2. It increases from 9.7% to 16.5% at 1,300 °C to 22.7–23.7% at 1,370 °C. Longer soak time results in larger shrinkage at low sintering temperatures. At 1,350 °C, complete sintering is observed. In $(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ ceramics of our another investigation, full shrinkage of 22.7% occurred at 1,330 °C by reaction-sintering process [34]. The influence of sintering temperature and soak time on the density of ST ceramics is shown in Fig. 3. Similar tendency as in shrinkage is observed. A density 4.99 g/cm^3 (97.5% of the theoretic value) is found after 6 h sintering at 1,370 °C. In the study of Kao and Yang, the relative density 95% was obtained in ST ceramics prepared from titanyl acylate precursor in a strong alkaline solution and sintered at 1,300 °C [35]. Zhi et al. reported 92–96% relative density in

$(\text{Sr}_{1-1.5x}\text{Bi}_x)\text{TiO}_3$ ceramics with $x = 0.0133\text{--}0.04$ were obtained at 1,380 °C [36]. This proved that high density ST ceramics could be produced by a reaction-sintering process.

The SEM photographs of as-fired ST ceramics sintered at 1,300 °C to 1,370 °C for 4 h and 6 h are illustrated in Fig. 4 and Fig. 5, respectively. Porous pellets with fine grains were formed at 1,300–1,330 °C and few pores formed at 1,350–1,370 °C. This result is consistent with the density value in Fig. 3. Grain size increases clearly with sintering temperature but not obviously with soak time. It is also observed that grain growth is slow even 6 h sintering at 1,300–1,330 °C. Mean grain size of ST ceramics are listed in Table 1. Grain size increased with temperature and soak time as expected. Grains $<1.5 \mu\text{m}$ were formed at 1,300–1,330 °C and of $2.2\text{--}3.3 \mu\text{m}$ at 1,350–1,370 °C. In the study of Zhi et al., the grain size is $2\text{--}4 \mu\text{m}$ in $(\text{Sr}_{1-1.5x}\text{Bi}_x)\text{TiO}_3$ ceramics [36]. Properties of ST based ceramics prepared by various processes are listed in Table 2 for comparison.

Fig. 5 SEM photographs of as-fired ST ceramics sintered at (a) 1,300 °C, (b) 1,330 °C, (c) 1,350 °C and (d) 1,370 °C for 6 h



BaTiO₃

All BT pellets sintered at 1,300–1,400 °C for 2–6 h are also of pure perovskite phase. The XRD patterns of BT ceramics sintered at 1,370 °C for 2–6 h are shown

in Fig. 6. The simple reaction-sintering process is again effective in preparing perovskite BT ceramics with the calcination bypassed. The shrinkage percentage of sintered BT pellets increases from 14.6% to 18.4% at 1,300 °C to 22.7–23.7% at 1,400 °C as illustrated in

Table 2 Properties of ST ceramics prepared by various methods

Proposed by	Zhi et al. [36]	Kao and Yang [35]	Liou et al. [34]	This work
Processing	(Sr _{1-1.5x} Bi _x)TiO ₃ Mixed oxide route	SrTiO ₃ titanyl acylate precursor	(Ba _{0.7} Sr _{0.3})TiO ₃ Reaction-sintering process	SrTiO ₃ Reaction-sintering process
Calcination temp.	1,050–1,100 °C	1,000 °C	No calcining	No calcining
Sintering temp./time	1,380 °C/2 h	1,300 °C/4 h	1330 °C/6 h	1370 °C/ 2–6 h
Shrinkage percentage	–	–	22.7%	22.7–23.7%
Density (g/cm ³)	92–96% T.D.	95% T.D.	98.9% T.D.	4.73–4.99 (92.4–97.5% T.D.)
Grain size (μm)	2–4	1–3	8.37	2.5–3.3
Dielectric constant (25 °C)	~650 (100 Hz)	410 (1 kHz)	4,400 (1 kHz)	290–310 (1 kHz)

T.D.: theoretic density

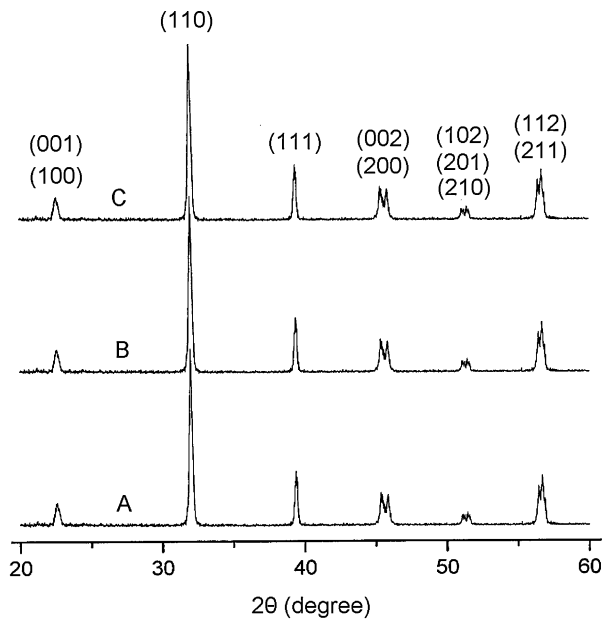


Fig. 6 XRD patterns of BT ceramics sintered at 1,370 °C for (a) 2 h, (b) 4 h and (c) 6 h

Fig. 7. Longer soak time results in larger shrinkage at low sintering temperatures the same as in ST ceramics. At 1,400 °C, full shrinkage percentage in BT ceramics reaches 23.7% for 4 h and 6 h soak time. For ST ceramics, shrinkage of 23.7% is found after 1,370 °C/6 h sintering. This implies a higher temperature is needed for full shrinkage in BT. While at 1,300 °C, higher shrinkage percentage is observed in BT than in ST. This indicates the densification process began at lower temperature in BT ceramics. In Fig. 8, the variation of density with sintering temperature and soak time is similar to that of shrinkage percentage. A density 5.89 g/cm³ (97.9% of the theoretic value 6.017) is found after 6 h sintering at 1,400 °C. As compared

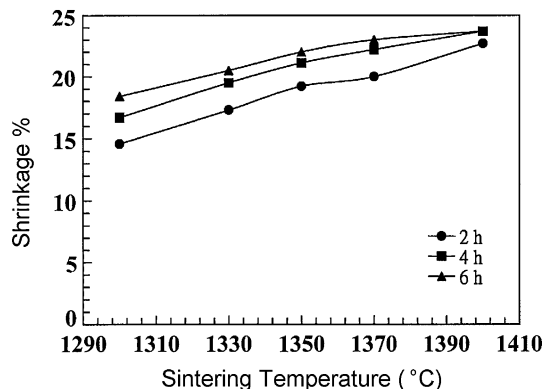


Fig. 7 Shrinkage percentage of BT ceramics sintered at various temperatures and soak time

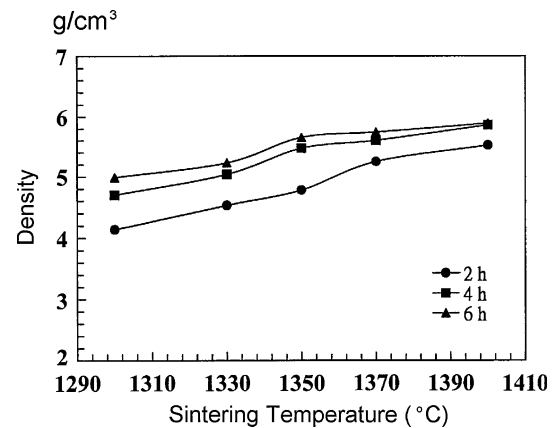
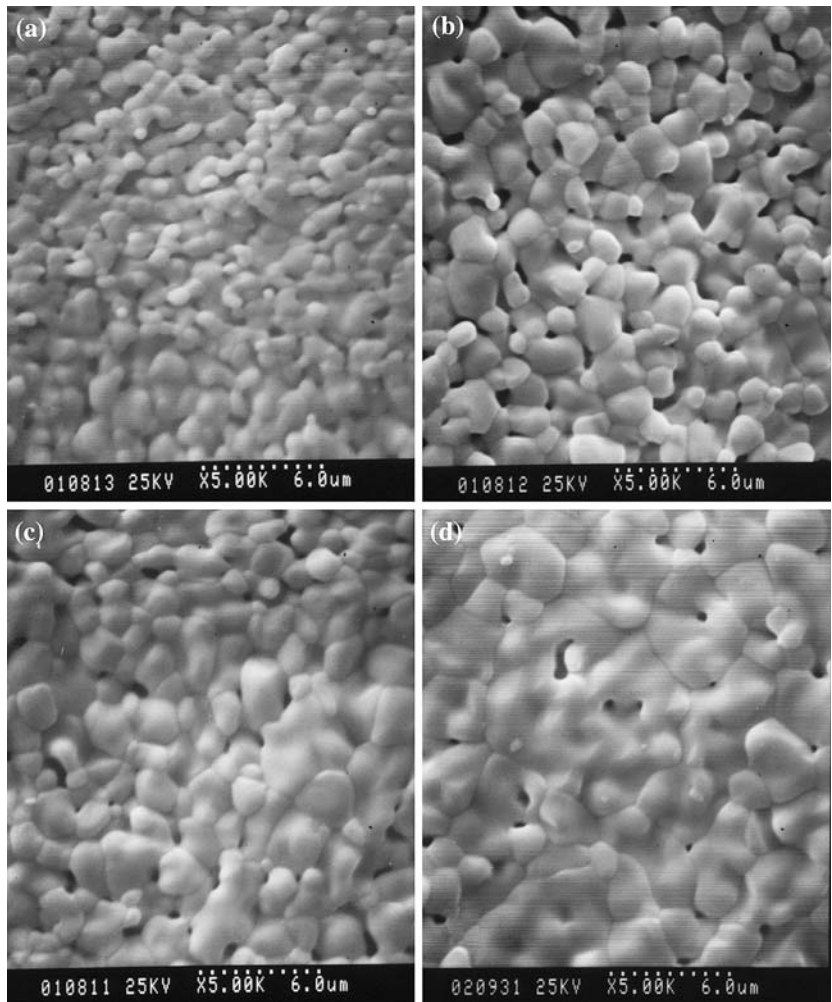


Fig. 8 Density of BT ceramics sintered at various temperatures and soak time

with other investigations, Caballero et al. obtained a value around 98% of theoretical density from a commercial grade BT raw material (ELMIC BT100, Rhone Poulenc S.A.) after sintered at 1,350 °C for 2 h [37]. Choi and Kang reported 97.1% after heated the 0.4 mol% TiO₂ added BaTiO₃ at 1,250 °C for 30 min in H₂ and sintered at 1,300 °C for 2 h [38]. Therefore, higher sintering temperature is needed for dense BT ceramics by a reaction-sintering process. Figure 9 shows the SEM photographs of as-fired BT ceramics sintered at 1,330 °C to 1,400 °C for 4 h. Fine grains of about 1 μm are observed in pellets sintered at 1,330 °C. These grains were merged to form larger conjoint grains. This may explain why the densification process began at lower temperature in BT than in ST ceramics as discussed previously. Grain size increases with sintering temperature and the grains were merged significantly. As the pellets were sintered for 6 h, the individual and conjoint grains become larger in Fig. 10. The amount of pores also decreased with increased temperature and soak time. In ST ceramics produced by reaction-sintering process, the grains just gathered closer and were not merged as illustrated in Figs. 4 and 5. While in Ba_{0.7}Sr_{0.3}TiO₃ ceramics, merged grains are also observed and the boundaries are clearly discerned [34]. The abnormal grain growth in BT ceramics has been reported [39–41]. These abnormal grains are usually very stable and remain unchanged during further heat-treatment. Lee et al. reported the microstructure consists of small matrix grains of about 2 μm and abnormally grown large grains of about 35 μm in BT sintered at 1,300 °C for 1 h. The fine matrix grains were completely replaced by a new set of abnormally grown coarse grains of about 70 μm as sintered at 1,355 °C for 1 h [41]. In Figs. 9 and 10, the merged grains are less than 10 μm. Therefore, the abnormal

Fig. 9 SEM photographs of as-fired BT ceramics sintered at (a) 1,330 °C, (b) 1,350 °C, (c) 1,370 °C and (d) 1,400 °C for 4 h



grain growth mode in BaTiO₃ system during sintering did not occurred in the BT ceramics produced by the reaction-sintering process. Dielectric constant at

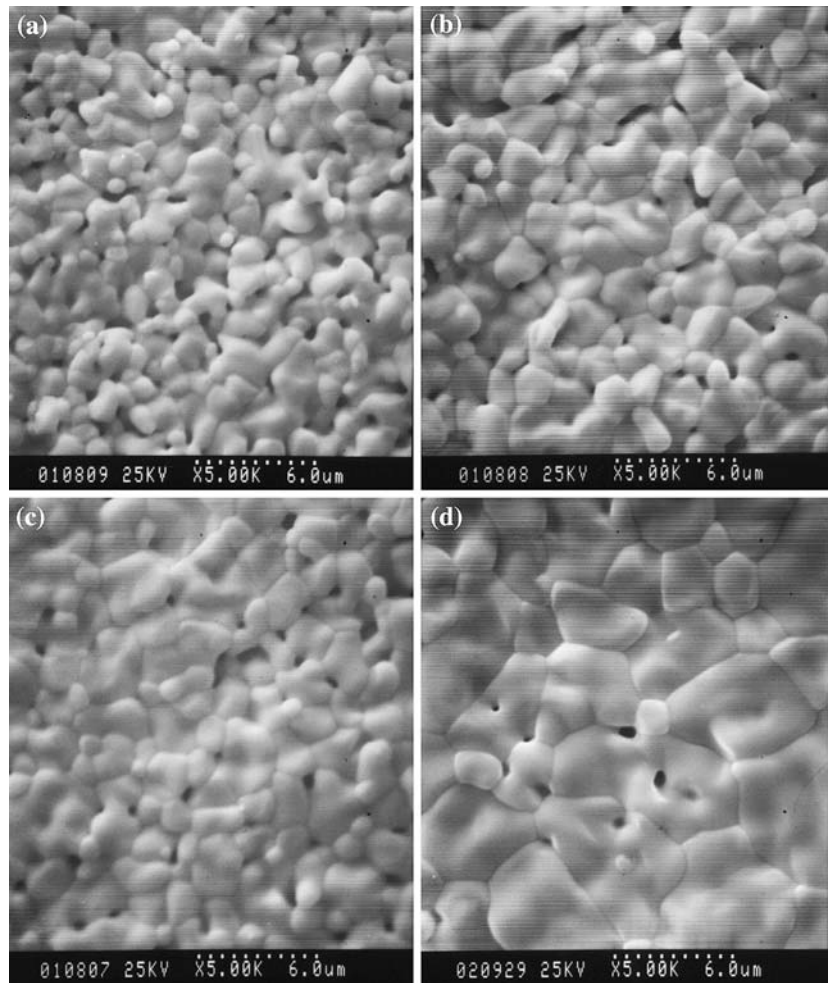
20–150 °C under 1–100 kHz of BT ceramics sintered at 1,400 °C for 6 h is shown in Fig. 11. Maximum value 10,420 is found at 125 °C under 1 kHz. It is also found

Table 3 Properties of BT ceramics prepared by various methods

Proposed by	Caballero et al. [37]	Choi and Kang [38]	Liou et al. [34]	This work
Processing	BaTiO ₃ commercial grade	BaTiO ₃ commercial grade	(Ba _{0.7} Sr _{0.3})TiO ₃ Reaction-sintering process	BaTiO ₃ Reaction-sintering process
Calcination temp.	ELMIC BT100, Rhone Poulenc S.A. 1,350 °C	1,250 °C/30 min in H ₂	No calcining	No calcining
Sintering temp./time	–	1,300 °C/2 h	1,330 °C/6 h	1,400 °C/6 h
Shrinkage percentage	–	–	22.7%	23.7%
Density (g/cm ³)	98% T.D.	97.1% T.D.	98.9% T.D.	5.89 (97.9% T.D.)
Grain size (µm)	–	1.51	8.37	–
Dielectric constant (maximum)	~7,500 (1 kHz) (sintered at 1,300 °C)	–	14,200 (1 kHz)	10,420 (1 kHz)

T.D.: theoretic density

Fig. 10 SEM photographs of as-fired BT ceramics sintered at (a) 1,330 °C, (b) 1,350 °C, (c) 1,370 °C and (d) 1,400 °C for 6 h



the dielectric constant of BT pellets decreased with sintering temperature and soak time. Properties of BT based ceramics prepared by various processes are listed in Table 3 for comparison.

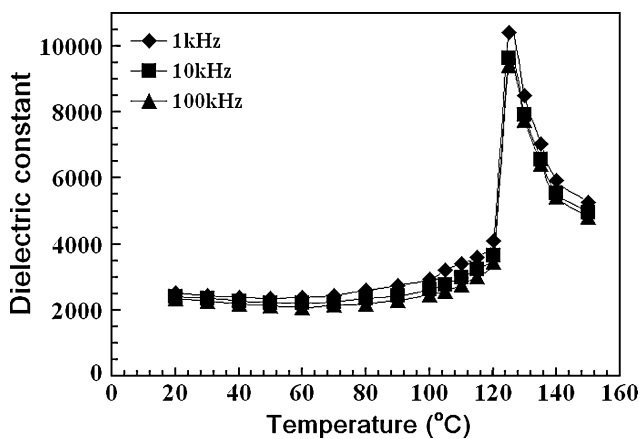


Fig. 11 Dielectric constant at 20–150 °C under 1–100 kHz of BT ceramics sintered at 1,400 °C for 6 h

Conclusions

Perovskite SrTiO_3 and BaTiO_3 ceramics were obtained by simple and effective reaction-sintering process successfully. A density 4.99 g/cm^3 (97.5% of the theoretic value) is found in SrTiO_3 after 6 h sintering at 1,370 °C. Grains $<1.5 \mu\text{m}$ formed at 1,300–1,330 °C and $2.2\text{--}3.3 \mu\text{m}$ at 1,350–1,370 °C SrTiO_3 . The densification process began at lower temperature in BaTiO_3 than in SrTiO_3 ceramics. A density 5.89 g/cm^3 (97.9% of the theoretic value) is found in BaTiO_3 after 6 h sintering at 1,400 °C. Merged grains are observed in BaTiO_3 and are less than $10 \mu\text{m}$ after sintered at 1,400 °C. The abnormal grain growth mode in BaTiO_3 system during sintering did not occurred in the BaTiO_3 ceramics produced by the reaction-sintering process.

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