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Synthesis and diffused phase transition of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics by a reaction-sintering process

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Abstract

$Ba_{0.7}Sr_{0.3}TiO_3$ (BST) ceramics prepared by a reaction-sintering process were investigated. BST ceramics could be obtained after 2–6 h sintering at 1330–1370 °C without any calcination involved. BST with density 5.68 g/cm^3 (99.8% of the theoretic value) was obtained at 1350 °C for 6 h sintering. Grains of 2–15 μm were formed after 2–6 h sintering at 1330–1370 °C. A diffused ferroelectric–paraelectric transition was observed in pellets sintered at 1330 °C for 2 h and disappeared at a longer soak time or a higher sintering temperature.

Keywords: BST; Dielectric; Reaction-sintering process

1. Introduction

Barium titanate ($BaTiO_3$; BT) ceramic is a typical ferroelectric material with Curie temperature around 130 °C. It is extensively used in multilayer ceramic capacitors (MLCCs) [1,2], positive temperature coefficient (PTC) thermistors [3] and piezoelectric transducers. As Sr^{2+} ions are partially substituted at Ba^{2+} ions in BT, the Curie temperature could be adjusted linearly in $Ba_xSr_{1-x}TiO_3$ (BST) system for $x < 0.75$ [4]. BST ferroelectrics exhibit high dielectric permittivity and have been widely investigated both in films and ceramics. BST thin films are promising materials for high-density dynamic random-access memories (DRAMs) [5,6]. BST ceramics are considered good candidates for applications in phased array antennas [7] as well as in capacitors, sensors and PTC thermistors [8–10].

In general, BT and BST ceramics are prepared by the conventional mixed oxide method 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 unsuitable for use as raw material for advanced electronic components. Therefore, other wet chemical processes including coprecipitation, oxalate, sol–gel and hydrothermal synthesis have been reported [11–13]. A novel mechanical activation process has been employed to produce BT powder [14,15]. In this mechanical technique, the powders of reactants are homogenized and activated in high-energy vibromill. Several ceramic materials such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $PbTiO_3$ and $Pb(Zr,Ti)O_3$ were also prepared by this process [16–18].

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. Liou et al. first produced lead magnesium niobate and lead iron niobate ceramics by a reaction-sintering process [19,20]. The mixture of PbO, $Mg(NO_3)_2$ (or $Fe(NO_3)_3$) and Nb_2O_5 was pressed and sintered directly into PMN and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics. These were the first successful syntheses of perovskite relaxor ferroelectric ceramics without having to go through the calcination step. PMN ceramics with a density of 8.09 g/cm^3 and dielectric constant 19,900 (1 kHz) are obtained. Other Pb-based complex perovskite ceramics [21–23] and some microwave dielectric ceramics such as $NiNb_2O_6$ and $BaTi_4O_9$ were also produced by this reaction-sintering process successfully [24,25].

In the present investigation, synthesis and dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics by a reaction-sintering process were reported.

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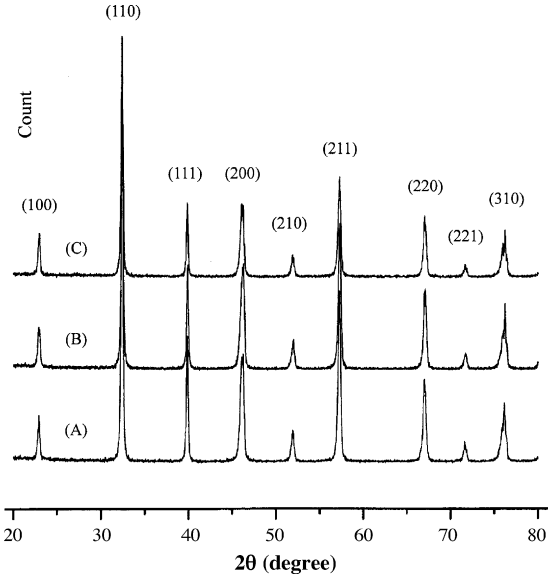

Fig. 1. XRD patterns of BST ceramics sintered at 1330–1370 °C for 4 h.

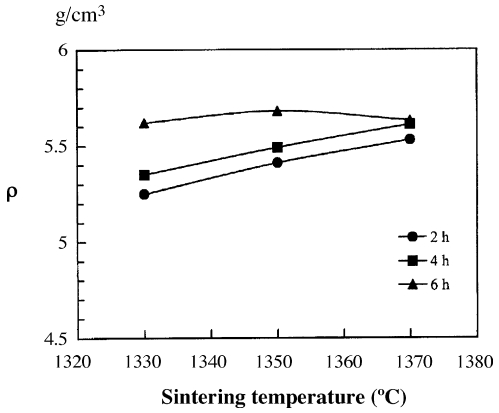

Fig. 2. Density of BST ceramics sintered at various temperatures and soak times.

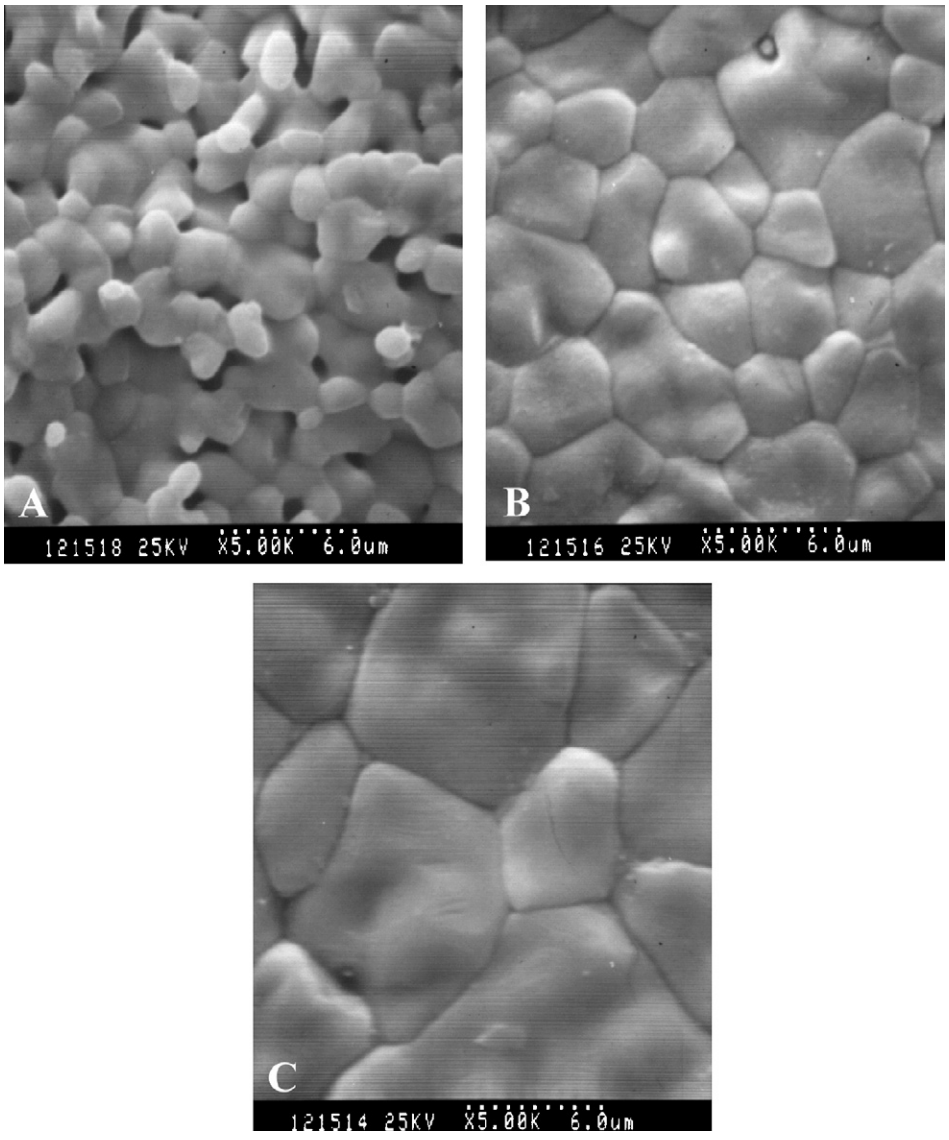

Fig. 3. SEM photographs of as-fired BST ceramics sintered at: (A) 1330 °C, (B) 1350 °C and (C) 1370 °C for 2 h.

2. Experimental procedure

All samples in this study were prepared from reagent-grade powders: $BaCO_3$ (99.9%), $SrCO_3$ (99%) and TiO_2 (99.9%). Appropriate amounts of raw materials for stoichiometric $Ba_{0.7}Sr_{0.3}TiO_3$ were milled in acetone with zirconia balls for 12 h. After the slurry was dried and pulverized the powder was pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were then heated at a rate 10 °C/min and sintered in covered alumina crucible at temperatures ranging from 1330 to 1370 °C for 2–6 h in air.

The sintered BST ceramics were analyzed by X-ray diffraction (XRD) to check the reflections of the phases. Microstructures were analyzed by scanning electron microscopy (SEM). The density of sintered BST pellets was measured by the Archimedes method. The dielectric constant was measured with the Agilent 4263B LCR meter.

3. Results and discussion

The XRD patterns of BST ceramics sintered at 1330–1370 °C for 4 h are shown in Fig. 1. From the patterns, single perovskite phase BST could be obtained by the reaction-sintering process. This indicates that the reaction-sintering process is a simple and effective method to produce BST ceramics. The influence of sintering temperature and soak time on the density of BST ceramics is illustrated in Fig. 2. Density increased with sintering temperature for 2 and 4 h soaked pellets. Density value reached 5.62 g/cm^3 after 6 h sintering at 1330 °C and increased to 5.68 g/cm^3 (99.8% of the theoretical

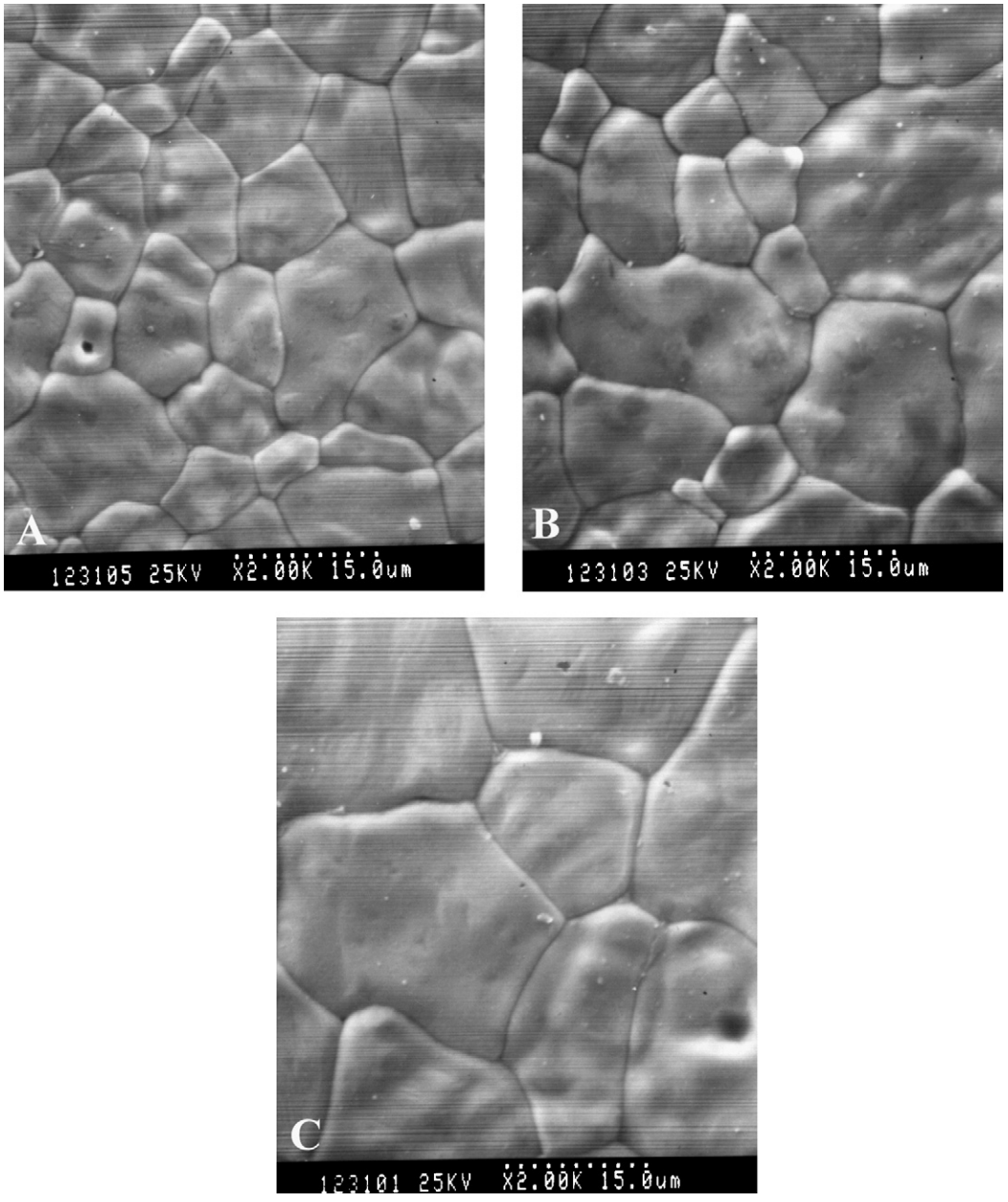

Fig. 4. SEM photographs of as-fired BST ceramics sintered at: (A) 1330 °C, (B) 1350 °C and (C) 1370 °C for 6 h.

Table 1
Shrinkage for BST ceramics sintered at various temperatures for 2–6 h

Sintering temperature (°C)	2 h (%)	4 h (%)	6 h (%)
1330	20.8	22.6	22.7
1350	22.1	22.6	22.7
1370	22.2	22.6	22.7

Table 2
Mean grain size of BST ceramics sintered at various temperatures for 2–6 h soak time (in μm)

Sintering temperature (°C)	2 h	4 h	6 h
1330	2.17	4.48	8.37
1350	3.44	5.73	9.67
1370	5.90	6.88	14.70

value) at 1350 °C. In the study of Rhim et al., 96.1% of the theoretical value was obtained in BST ceramics prepared by boron-containing liquid-phase sintering [26]. This proved that high-density BST ceramics could be produced by a reaction-sintering process.

The shrinkage results for BST ceramics are listed in Table 1. The shrinkage increased with soak time and reached 22.7% for 6 h. It is also observed that the shrinkage increased with sintering temperature for 2 h soaked pellets. For 4 and 6 h, full shrinkage occurred at 1330 °C. This indicated that sintering was not completed at 2 h. As compared with BST ceramics reported by Rhim et al. [26], 1100 °C/2 h calcined BST reached a full shrinkage of 14% at 1300 °C. Higher shrinkage was obtained in BST ceramics prepared by the reaction-sintering process. The green pellets composed of a mixture of raw materials rather than a calcined powder may be the major reason.

The SEM photographs of as-fired BST ceramics sintered at 1330–1370 °C for 2 h are illustrated in Fig. 3. Porous pellet was formed at 1330 °C and the pores disappeared at 1350 and 1370 °C. This result is consistent with the density value for 2 h sintered BST pellets in Fig. 3. In Fig. 4, dense BST ceramics were obtained after 6 h sintering at 1330–1370 °C. Grain size increased with sintering temperature in BST ceramics. The mean grain sizes of BST ceramics are listed in Table 2. Grain size increased with temperature and soak time as expected. In the study of Jeon, abnormal grain growth was observed and the microstructure showed a bimodal structure consisting of

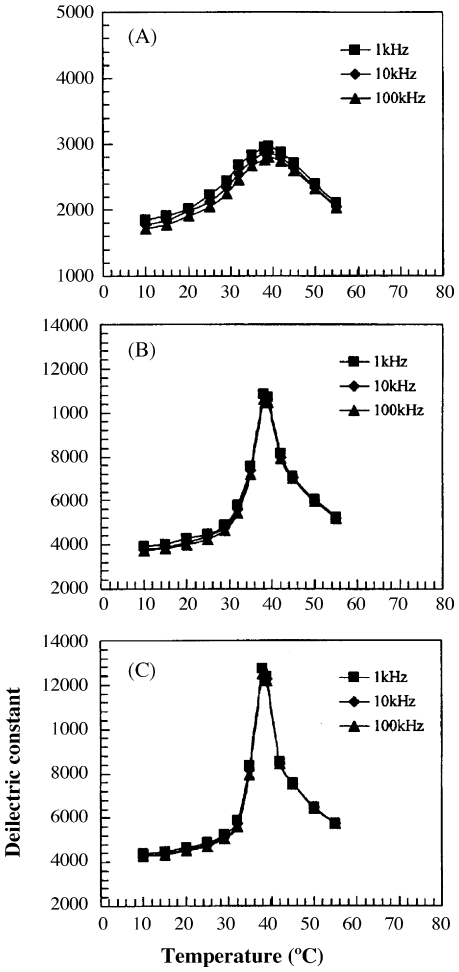

Fig. 5. Temperature dependence of the dielectric constant at various frequencies for the BST ceramics sintered at: (A) 1330 °C, (B) 1350 °C and (C) 1370 °C for 2 h.

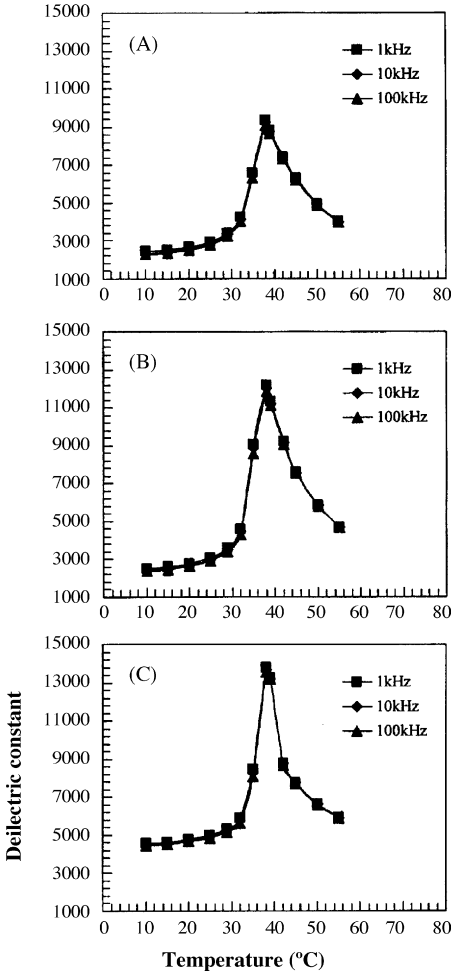

Fig. 6. Temperature dependence of the dielectric constant at various frequencies for the BST ceramics sintered at: (A) 1330 °C, (B) 1350 °C and (C) 1370 °C for 4 h.

abnormally growing grains and fine matrix grains in $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics sintered at 1350 °C for 1 h [27]. Exaggerated grain growth occurred with grains as large as 10 μm in BST ceramics sintered at 1300 °C/2 h was also reported by Hayashi et al. [28]. In the BST films investigated by Guo et al., pores larger than grains were observed and the grain sizes (5–10 μm) became fairly uniform as the sintering time increased from 2 to 8 h at 1350 °C [29]. Therefore, the abnormal grain growth mode usually observed in $BaTiO_3$ systems during sintering did not occur in the BST ceramics produced by the reaction-sintering process.

The temperature dependence of the dielectric constant at various frequencies (*K–T* curve) for the BST ceramics sintered at 1330–1370 °C for 2 h is shown in Fig. 5. The Curie temperature is found at about 40 °C. The peak value increased with sintering temperature (3000 at 1330 °C and 13,000 at 1370 °C) and a diffused ferroelectric–paraelectric transition were observed in the BST ceramics sintered for 1330 °C. The increased peak value is resulted from the increased density and grain size. The diffused transition disappeared at 1350 and 1370 °C. A transition broadening was also observed in BST ceramics prepared by boron-containing liquid-phase sintering [26] and in bismuth doped $Ba_{1-x}Sr_xTiO_3$ ceramics with $x = 0.2–0.8$ by the conventional mixed oxide method [30]. In the study of Jeon, the transition broadening appeared in 1350 °C/1 h sintered $Ba_{1-x}Sr_xTiO_3$ ceramics with $x = 0.4–0.6$ and disappeared when sintered at 1450 °C/1 h. This may have resulted from the fine matrix grains formed in the pellets with $x \geq 0.4$ at 1350 and 1400 °C sintering. At 1450 °C, fine matrix grains were not observed even with $x = 0.6$. The transition broadening was not observed as the fine matrix grains disappeared [27]. This could be the reason why the diffused transition disappeared at 1350 and 1370 °C in Fig. 5.

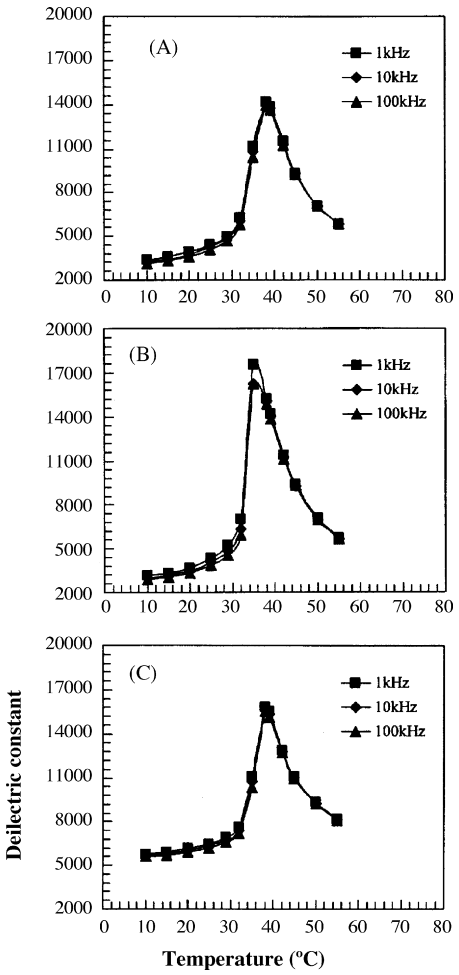

Fig. 7. Temperature dependence of the dielectric constant at various frequencies for the BST ceramics sintered at: (A) 1330 °C, (B) 1350 °C and (C) 1370 °C for 6 h.

Fine grains about 2 μm were observed at 1330 °C/2 h sintering and grains of 3.44 μm formed after 1350 °C/2 h sintering as listed in Table 2. Hench and West proposed that the ferroelectric transition of BT is gradual in the case of fine particles (1–2 μm). This is different from the extremely sharp transition in the single crystalline BT. They thought there is a relationship between the size of the crystalline structure and the equilibrium positions of titanium ions in the polarized state. The increase in dielectric constant at Curie temperature is much less for ultrafine particles (0.2 μm). The domain orientation in an ultrafine powder is random and this tends to broaden the ferroelectric transition [31]. The diffused transition was not observed in BST ceramics sintered at 1330–1370 °C for 4 h in Fig. 6. The peak dielectric constant increased from 9200 at 1330 °C to 14,000 at 1370 °C. The *K–T* curves of BST ceramics sintered at 1330–1370 °C for 6 h are shown in Fig. 7. Normal ferroelectric *K–T* curves are observed.

4. Conclusion

Perovskite $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics could be obtained successfully by a simple and effective reaction-sintering process. Density increased with sintering temperature for 2 and 4 h soak time at 1330–1370 °C. A density of 5.68 g/cm^3 (99.8% of the theoretical value) was obtained at 1350 °C/6 h sintering. Grains of 2–15 μm were formed after 1330–1370 °C sintering for 2–6 h. A diffused ferroelectric–paraelectric transition was observed in pellets sintered at 1330 °C for 2 h and not observed at a longer soak time or a higher sintering temperature.

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