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Research Article

Microstructural and Electrical Properties of Sn-Modified $BaTiO_3$ Lead-Free Ceramics by Two-Step Sintering Method

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$Ba(Ti_{0.92}Sn_{0.08})O_3$ lead-free ceramics were prepared using a two-step sintering (TSS) technique. Varying the first sintering temperature T_1 (1400 and 1500°C) and the dwell time t_1 (0, 15, and 30 min), we obtained dense ceramics which were then soaked at a constant temperature of 1000°C (T_2) for 6 h (t_2). The structural and electrical properties were investigated. XRD results indicated that all the ceramics showed a pure perovskite phase with tetragonal symmetry. Density and grain size increased with higher T_1 temperatures and increased t_1 dwell times. Enhanced electrical properties were achieved by sintering at the optimized T_1 sintering temperature and t_1 dwelling time. At the lower T_1 sintering temperature of 1400°C, the dielectric and piezoelectric properties and the Curie temperature of the ceramics were improved significantly by increasing t_1 dwell time. Further, increasing the sintering temperature T_1 to 1500°C, excellent properties were obtained at $t_1 = 15$ min which then deteriorated when t_1 was increased to 30 min. The electrical properties of the sample sintered under the $T_1/t_1/T_2/t_2$ condition of "1500/15/1000/6" showed the best values. For this sample the piezoelectric coefficient (d_{33}), dielectric permittivity (ε_r), loss factor ($\tan\delta$), and Curie temperature (T_C) were 490 pC/N, 4385, 0.0272, and 48°C, respectively.

1. Introduction

Because of the high toxicity of lead oxide, the use of Pb $(Zr_xTi_{1-x})O_3$-based materials has caused serious environmental problems. Hence, the development of piezoelectric materials has focused considerable attention in recent years on lead-free materials which exhibit highly piezoelectric properties [1–4]. Barium titanate ($BaTiO_3$) is a lead-free ferroelectric material currently used to replace Pb $(Zr_xTi_{1-x})O_3$ piezoelectric ceramics in electronic devices ($d_{33} = 191$ pC/N) [3]. It is a typical ferroelectric material with a tetragonal symmetry of perovskite structure at room temperature [5]. It is known that an appropriate amount of doping into the $BaTiO_3$ can produce piezoelectricity comparable with $Pb(Zr_xTi_{1-x})O_3$-based ceramics [5–9]. Among modified $BaTiO_3$ composites, barium stannate titanate ($BaTi_{1-x}Sn_xO_3$) can modify both the microstructure and electrical properties of $BaTiO_3$ [9]. Enhanced piezoelectric properties have been reported for $Ba_{0.90}Ca_{0.10}Ti_{1-x}Sn_xO_3$ ceramics with a super-high d_{33} (521 pC/N) at $x = 0.10$ [10]. However, the densification of $Ba_{0.90}Ca_{0.10}Ti_{1-x}Sn_xO_3$ ceramics requires sintering for 2 h at temperatures above 1400°C, which is too high for low-temperature cofired ceramics (LTCC) processing.

The two-step sintering process is heating rate-controlled and effectively densifies the ceramics at lower temperatures. For this method, samples are heated to a higher temperature (T_1) and held at T_1 for a short time t_1, then the temperature is immediately lowered to a soaking temperature, T_2. The process can eliminate pores and reduce the volatilization of the low melting point substances [11]. In the present work, $Ba(Ti_{1-x}Sn_x)O_3$ ceramics at $x = 0.08$ were fabricated using the two-step sintering method to control grain growth, and the effects of sintering temperature and dwell time on the

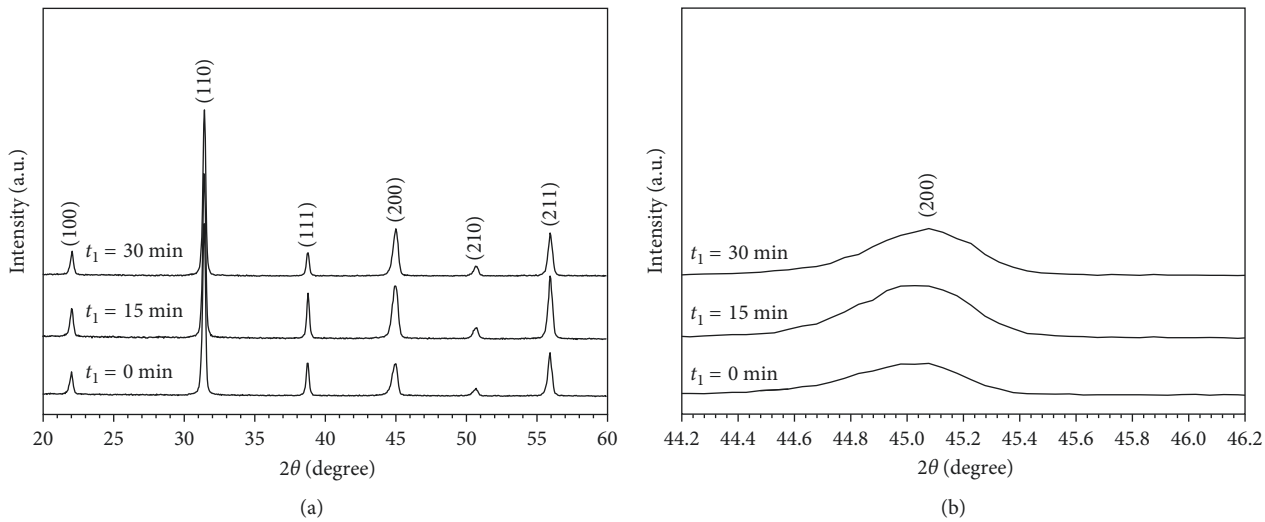

Figure 1: (a) XRD patterns of BTS samples sintered at different dwelling times, t_1, and (b) the expanded XRD patterns in the 2θ range of 44.2–46.2 of BTS ceramics.

phase structure, microstructure, and electrical properties of the fabricated ceramics were systematically investigated.

2. Materials and Method

$Ba(Ti_{1-x}Sn_x)O_3$ (abbreviated as BTS: $x = 0.08$) lead-free ceramics were synthesized by a solid-state method using $BaCO_3$ (99.9%), TiO_2 (99.9%), and SnO_2 (99.9%) as raw materials. All starting powders were ball milled in alcohol using zirconia balls for 24 h. After calcination at 1200°C for 2 h, the obtained powders were uniaxially pressed into disk-shaped compacts and then sintered using a two-step sintering method with the following profile. The green samples were first heated from room temperature to 900°C at a slow heating rate of 5°C/min and then to the sintering temperature T_1 of either 1400 or 1500°C at a heating rate of 10°C/min and held for a short dwell time (t_1) of 0, 15, or 30 min. To realize the desired final density and to control grain growth, the soaking temperature of the second stage, T_2, was set lower than T_1 at 1000°C with a cooling rate of 20°C/min, and the soaking time (t_2) at T_2 was 6 h. The symbols "$T_1/t_1/T_2/t_2$" are used to indicate the two-step sintering conditions.

The crystalline phases of the sintered samples were characterized with a powder X-ray diffractometer (XRD, X'Pert MPD, Philips) with CuKα radiation generated at 40 kV and 30 mA. The density of the sintered samples was measured using a water immersion method in accordance with Archimedes' principle. The microstructure of the ceramic surfaces was examined by scanning electron microscopy (SEM, Quanta400, FEI). The intercept method was used to determine the average grain size. For electrical characterizations, the ceramic samples were carefully polished and painted with silver paste on both sides. The dielectric properties were measured using a high precision LCR meter (LCR 821, GW INSTEK) from 25°C to 200°C at a heating rate of 3°C/min. To measure their piezoelectric properties, the ceramic samples were poled at room temperature (25°C) for 20 min under an electric field of 1.0–4.0 kV/mm in a silicone oil bath. The piezoelectric coefficient d_{33} was measured by a piezo-d_{33} meter (YE2730A d_{33} meter, APC International, Ltd.).

3. Results and Discussion

Figure 1 shows the XRD patterns of BTS samples sintered under "1500/t_1/1000/6" conditions with different t_1 dwell times of 0, 15, and 30 min at room temperature. It can be observed that all sintered samples showed a single perovskite structure with a tetragonal phase indicating that Sn^{4+} diffused into $BaTiO_3$ lattices during sintering. The diffraction peaks showed slightly sharper at t_1 of 15 min indicating an enhancement of crystallinity in the samples. Moreover, the intensity of the (111) diffraction peak of the sample sintered at $t_1 = 15$ min was stronger than for other samples. The expanded XRD patterns of BTS ceramics in the 2θ range of 44.2–46.2° showed that the peak position shifted slightly to a higher angle with increasing dwell time t_1, Fig. 1(b). In part this difference may relate to strain effects. The lattice parameters for samples with dwell time $t_1 = 0$ and 15 min were $a = 4.0232$ and $c = 4.0402$ Å, whereas for samples with dwell time $t_1 = 30$ min, they were $a = 4.0190$ and $c = 4.0446$ Å. It can also be seen that the intensity of the XRD peaks slightly decreased in response to decreased crystalline phase content, as well as increased lattice strain when t_1 was increased to 30 min. Average crystallite size was calculated from the Debye–Scherrer formula [12]:

$$D = \frac{0.9\lambda}{\beta\cos\theta}, \quad (1)$$

where D is crystallite size, λ is X-ray wavelength (0.15406 nm), β is full width at half maximum (FWHM) of peak in radians, and θ is Bragg's angle. The average crystallite size increased with increasing dwell time up to 15 min and

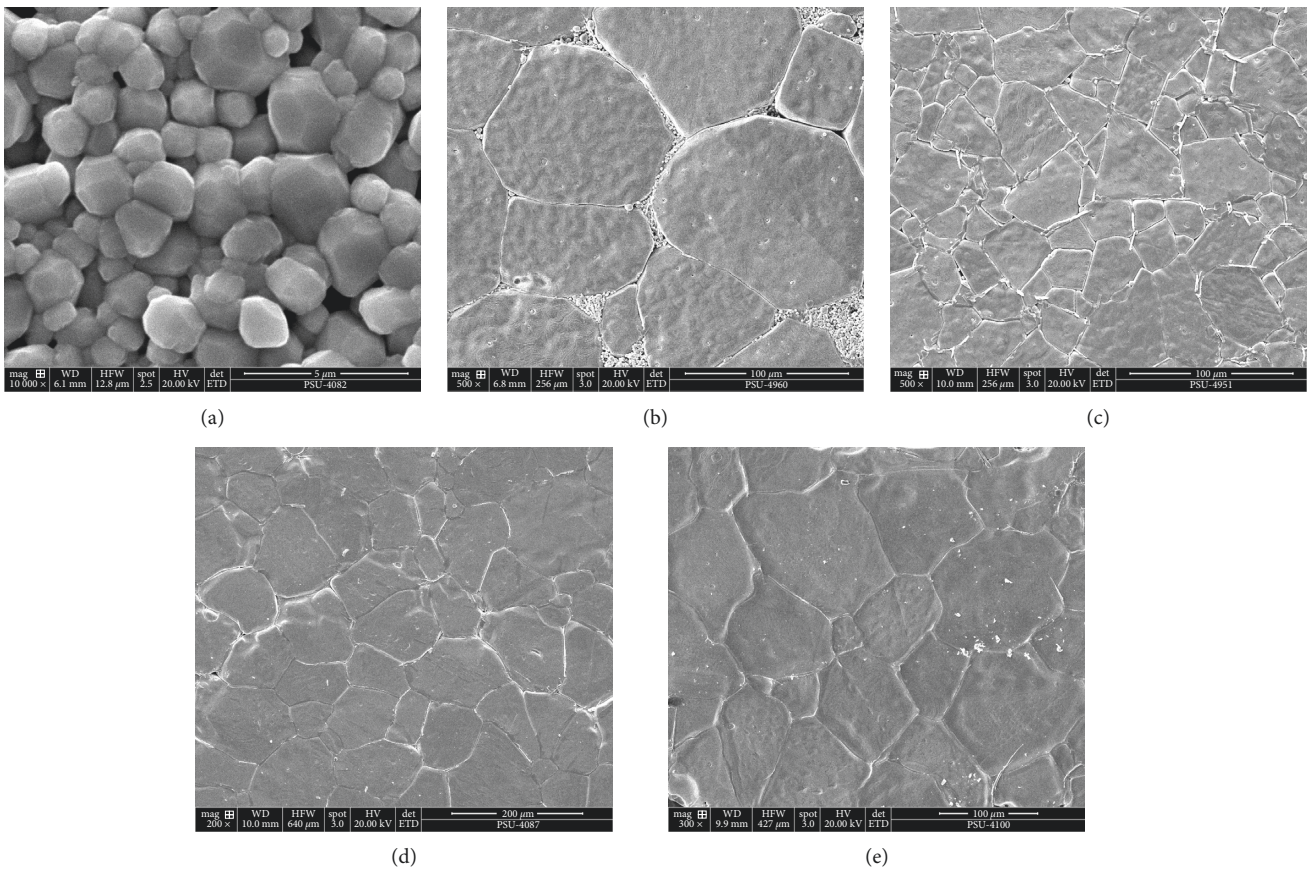

Figure 2: SEM micrographs of the BTS ceramics sintered under the various conditions: (a) "1400/15/1000/6"; (b) "1400/30/1000/6"; (c) "1500/0/1000/6"; (d) "1500/15/1000/6"; (e) "1500/30/1000/6".

Table 1: The bulk density, ε_r, and tanδ at room temperature (RT), $\varepsilon_{r,\max}$ and $\tan_{\delta,\max}$ at Curie temperature (T_C), and T_C at 1 kHz, grain size, and piezoelectric coefficient (d_{33}) of the BTS samples.

Sintering conditions $T_1/t_1/1000/6$		Bulk density (g/cm^3)	$\varepsilon_{r,RT}$	$\tan_{\delta,RT}$	$\varepsilon_{r,\max}$	$\tan_{\delta,\max}$	T_C (°C)	Grain size (μm)	d_{33} (pC/N)
T_1 (°C)	t_1 (min)								
1400	0	4.86 ± 0.02	*	*	*	*	*	*	*
	15	5.60 ± 0.05	4085	0.0291	9729	0.0126	41	1.4 ± 0.4	35
	30	5.82 ± 0.05	4301	0.0776	16730	0.0248	44	43.2 ± 4.6	47
1500	0	5.88 ± 0.03	4091	0.0766	19832	0.0208	42	20.1 ± 3.4	260
	15	5.90 ± 0.01	4385	0.0272	18601	0.0203	48	30.1 ± 6.0	490
	30	5.85 ± 0.02	3564	0.0738	17950	0.0127	47	47.8 ± 7.9	301

*Ceramic sample could not be achieved by sintering under conditions of 1400/0/1000/6.

then remained constant as the value of t_1 further increased to 30 min. It was found to be 34.2, 42.8, and 42.8 nm for dwell time $t_1 = 0$, 15, and 30 min, respectively.

Figure 2 shows the microstructure of the BTS samples sintered under conditions of "$T_1/t_1/1000/6$" ($T_1 = 1400$ and 1500°C; $t_1 = 0$, 15, and 30 min). The SEM micrographs indicate that the microstructure is dependent on the sintering profile. At the lower sintering temperature ($T_1 = 1400$°C) without dwell time ($t_1 = 0$ min), well-sintered samples could not be obtained (SEM micrograph is not shown). At a dwell time of 30 min, the grain size increased rapidly and exhibited an abnormal grain growth. A relatively uniform grain size of 20.1 ± 3.4 μm could be achieved for samples sintered under the "1500/0/1000/6" condition. It is evident that the increase in the sintering temperature, T_1, and dwelling time, t_1, helped to promote grain growth. This is because the higher sintering temperature and dwell time can enlarge the diffusion coefficient and make grain boundary migration easier [8].

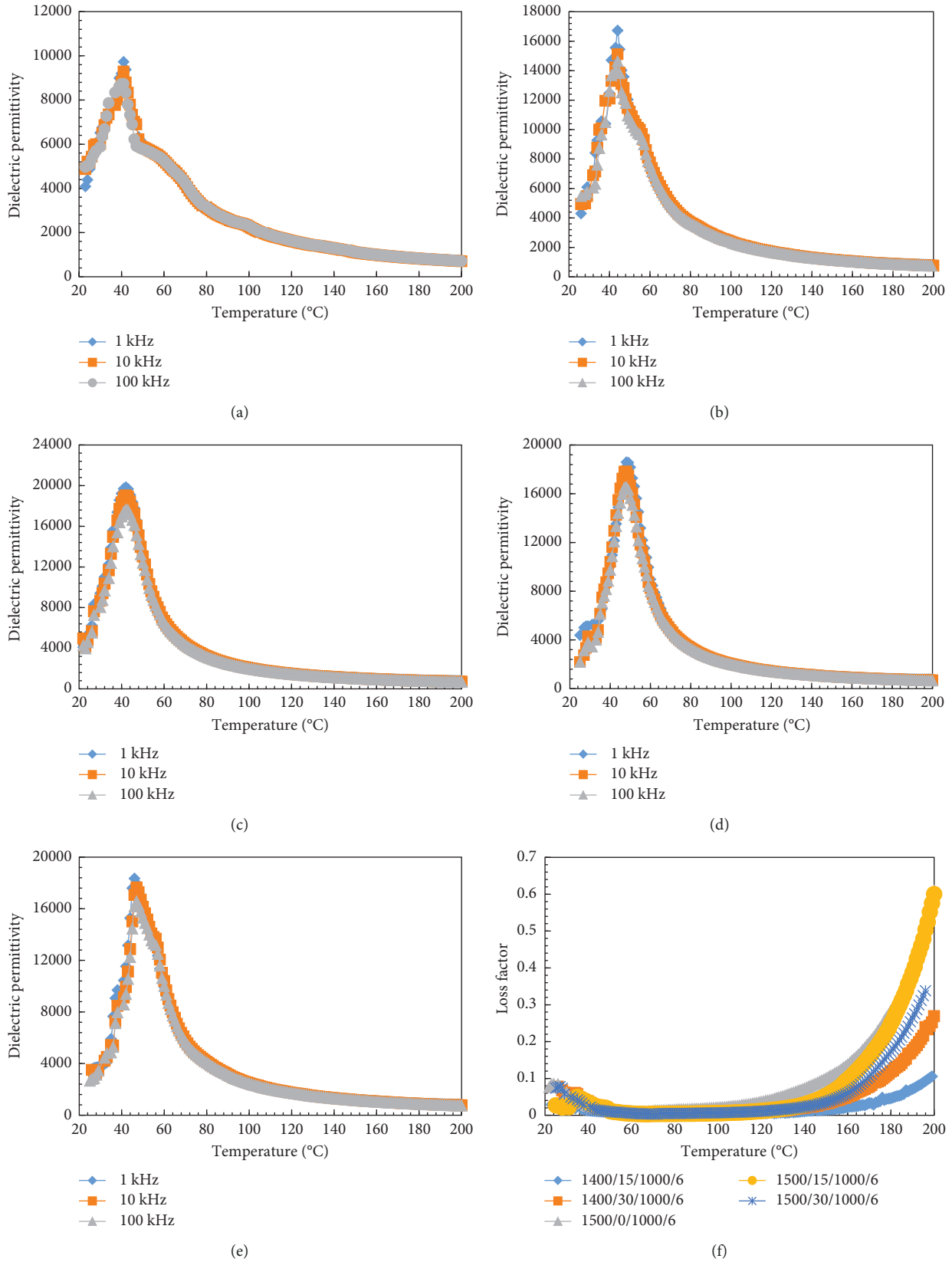

Figure 3: The temperature dependence of dielectric permittivity of BTS ceramics sintered at different conditions at frequencies of 1, 10, and 100 kHz: (a) "1400/15/1000/6"; (b) "1400/30/1000/6"; (c) "1500/0/1000/6"; (d) "1500/15/1000/6"; (e) "1500/30/1000/6"; (f) loss factor (tanδ) of the BTS ceramics at 1 kHz.

In the present case, increasing the sintering temperature and dwell time improved densification as well as the grain growth. It can be seen in Table 1 that when the sintered samples underwent the same dwell time, t_1, the bulk densities were increased by increasing the sintering temperature T_1, whereas when the samples were sintered at the same sintering temperature T_1, improvements in the relative density were recorded with correspondingly longer dwell times, t_1. The optimal value of t_1 dwell time depended significantly on the sintering temperature, T_1. The highest density of 5.90 ± 0.01 g/cm^3 was obtained when $t_1 = 15$ min, and the density was slightly lower when $t_1 = 30$ min. The densification of the BTS samples improved significantly at the higher sintering temperature T_1 with the longer dwell time t_1. In general, the two-step sintering technique not only effectively densified the ceramics, but also enabled sintering at a reduced temperature. For this work, the soaking temperature T_2 was set at a low temperature of 1000°C. At higher temperatures and longer dwell times, grain boundary migration causes grain growth, while grain boundary diffusion can still be activated causing enhanced density [13]. However, the density of the samples decreases if the dwell time exceeds the dwell time of the optimum sintering condition ("1500/30/1000/6"). Longer dwell time greatly influenced the porosity of the surface oxide layer with the surface getting more porous.

Figure 3 shows the temperature dependence of dielectric properties of the BTS ceramics as a function of sintering temperature, T_1, and dwell time, t_1. Increasing the sintering temperature and dwell time clearly increased the values of $\varepsilon_{r,\mathrm{RT}}$ up to the maximum value of 4385, which was attained when T_1 was 1500°C and the dwell time 15 min. The value of $\varepsilon_{r,\mathrm{RT}}$ then decreased when t_1 was increased to 30 min. This is due to an increase in grain size. The low dielectric loss of ≤2% indicated that these BTS ceramics sintered under two-step conditions are promising for practical applications. The temperature dependence of the dielectric permittivity (ε_r) of the BTS ceramics was also determined in order to characterize their phase transition behavior, as shown in Figure 3. The sintering temperature and dwell time also affected the Curie temperature. It can be seen that the tetragonal-cubic (or Curie temperature T_C) phase transition temperatures all increased slightly at the higher sintering temperatures, T_1, and longer dwell times, t_1. The T_C is shown in Table 1 as $T_{\max}$ which showed the maximum value of dielectric permittivity. Since the sintering temperature and the dwell time (T_1, t_1) change the microstructure of ceramics, they have an important influence on the tetragonal-cubic phase transition temperature. It can be seen that the samples with bigger grain sizes exhibited higher T_C values. This is attributed to the increased proportion of tetragonal phase and increased ferroelectricity of the ceramics. This result is consistent with other perovskite structure ceramics [14, 15]. The piezoelectric coefficient d_{33} as a function of sintering temperature, T_1, and dwell time, t_1, for the BTS ceramics, is also shown in Table 1. The d_{33} value increased with increasing sintering temperatures and dwell times, reached a maximum value of 490 pC/N at the "1500/15/1000/6" condition and then decreased at a dwell time of 30 min. At the longer dwell time, deflection in the stoichiometric composition and deterioration in the microstructure degraded the piezoelectric properties of the sample.

4. Conclusions

Two-step sintering was used to fabricate dense Ba(Ti, Sn)O_3 ceramics at low sintering temperatures. The microstructural and electrical properties of the $Ba(Ti_{0.92}Sn_{0.08})O_3$ ceramics are obviously dependent on the sintering temperature (T_1) and the dwelling time (t_1). Under the optimal condition of "1500/15/1000/6," the dense samples had an average grain size of approximately 30 μm and showed good dielectric and piezoelectric properties. Values for the piezoelectric constant (d_{33}), relative permittivity (ε_r), loss factor (tanδ), and Curie temperature (T_C) were 490 pC/N, 4385, 0.0272, and 48°C, respectively.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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