

Article

Effect of Microwave Sintering on the Properties of $0.95(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3-0.05(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ Ceramics

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Received: 21 January 2019; Accepted: 21 February 2019; Published: 8 March 2019



Abstract: Perovskite ceramics are a common microwave dielectric material, but the development and application of this material has been limited by the high, positive resonance frequency temperature coefficient and sintering temperature. Therefore, adjusting the temperature coefficient of the resonance frequency and reducing the sintering temperature have become important research directions. In this work, $0.95(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3-0.05(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics (referred to as 0.95CST-0.05BNT) were prepared by standard solid-state reaction and microwave sintering. Microwave sintering greatly shortened the sintering period and holding time. Moreover, the 0.95CST-0.05BNT ceramics showed more uniform grain size distribution, and microwave sintering reduced energy consumption in the experiment. Therefore, the temperature coefficient of the resonance frequency of MWS ceramics was reduced by $119 \times 10^{-6} / ^\circ\text{C}$. All of the ceramics, which were sintered at $1300\text{ }^\circ\text{C}$ for 40 minutes, showed optimal microwave dielectric properties: $\epsilon_r = 187.6$, $Q \times f = 8958\text{ GHz}$, and $\tau_f = +520 \times 10^{-6} / ^\circ\text{C}$.

Keywords: dielectric properties; microwave sintering; temperature coefficient; ceramics

1. Introduction

With the rapid development of wireless communication technology, microwave dielectric materials have been extensively used in many microwave-integrated circuits, such as dielectric oscillators, filters, and other devices [1]. Generally, microwave dielectric ceramics require three key properties, including dielectric constant (ϵ_r), a high $Q \times f$ value, and a low-temperature coefficient of resonance frequency (τ_f) to maintain the temperature stability of microwave ceramics [2,3]. Owing to their high dielectric properties, the microwave ceramics have been in high demand in recent years.

Recently, many perovskite ceramics have attracted much attention due to their good dielectric properties and the adjustable nature of the perovskite structure [4]. Examples include $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ceramics ($\epsilon_r = 218$, $Q \times f = 7182\text{ GHz}$, $\tau_f = +1164 \times 10^{-6} / ^\circ\text{C}$), CaTiO_3 ceramics ($\epsilon_r = 174$, $Q \times f = 6005\text{ GHz}$, $\tau_f = +824 \times 10^{-6} / ^\circ\text{C}$) [5], and $(\text{Ca}_{0.2}\text{Sr}_{0.8})_3\text{Ti}_2\text{O}_7$ ceramics ($\epsilon_r = 58$, $Q \times f = 25727\text{ GHz}$, $\tau_f = +359 \times 10^{-6} / ^\circ\text{C}$) [6]. $(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3$ ($\epsilon_r = 173$, $Q \times f = 8310\text{ GHz}$, $\tau_f = +942 \times 10^{-6} / ^\circ\text{C}$) ceramics which, have a large positive τ_f value, have been widely studied; meanwhile, $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$, which has a negative τ_f value of $-180 \times 10^{-6} / ^\circ\text{C}$ and a higher dielectric constant of 480, is often used as an auxiliary material [7–9]. Thus, $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ is added to $(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3$ to compensate for its τ_f . In our previous work, $(1-x)(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3-x(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics were prepared by the standard solid-state sintering method. The 0.95CST-0.05BNT ceramics, having excellent performance ($\epsilon_r = 185.5$, $Q \times f = 8116\text{ GHz}$, $\tau_f = +639 \times 10^{-6} / ^\circ\text{C}$), had been obtained [10].

Nowadays, the microwave sintering of ceramic materials is a new type of sintering process both at home and abroad [11,12]. The basic heating principle of microwave sintering is quite different from that of conventional sintering. During the microwave heating, the polarization occurs inside the material, which makes the dipole turn repeatedly with the fast-changing alternating electromagnetic field. Since the frequency of the magnetic field changes very fast, the vibration and friction between the dipoles in the material become more intense; thus, the material itself heats up and warms up to a certain temperature. Compared with conventional sintering methods, we summarize the characteristics of several microwave sintering methods as follows. 1. Due the effect of the electromagnetic field, the material is heated by itself. The overall heating of the material is more uniform; in addition, the heating method avoids the additional internal stress produced by uneven heating, and reduces the internal defects of the materials, which reduces the material loss and makes the material difficult to crack due to fast speed of the heating process. 2. Microwave sintering can greatly shorten the sintering cycle, increase the sintering rate, and reduce the sintering temperature to obtain ceramics with high densification. At the same time, microwave sintering can optimize the properties of materials. 3. Microwave sintering can optimize the microstructures of materials. Since the heating rate is very fast during microwave sintering, it can effectively inhibit grain growth, which can successfully prepare a nanometer-level superfine powder.

In this paper, 0.95CST–0.05BNT ceramics were prepared by standard solid-state and microwave sintering. The microwave sintering method has the advantages of a short sintering period and low energy consumption. The effect of microwave sintering on microstructures and properties were presented and discussed. Finally, we summarized the differences between microwave sintering (MWS) and conventional sintering (CS) in a table. Microwave sintering greatly shortened the sintering period and reduced the energy consumption.

2. Experimental

AR raw powders of CaCO_3 (Shanghai Aladdin Biochemical Technology Co., Ltd. Shanghai, China), SrCO_3 (China Pharmaceutical Group Chemical Reagents Co., Ltd. Shanghai, China), Bi_2O_3 (Xilong Science Co., Ltd. Shantou, China), Na_2CO_3 (Yixing Chemical Reagent Factory, Yixing, China), and TiO_2 (Xiantao Zhongxing Electronic Materials Co., Ltd. Xiantao, China) (>99%) were weighed according to the stoichiometric ratio of $(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3$ and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$. The $(\text{Ca}_{0.88}\text{Sr}_{0.12})\text{TiO}_3$ powders were milled for six hours with ZrO_2 balls and deionized water. The $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ powders were milled for six hours with ZrO_2 balls and ethanol. The ball-milling parameters were as follows: power-to-ball weight ratio: 1:2; powder-to-water weight ratio: 1:1.5; powder-to-ethanol weight ratio: 1:1.2. Afterwards, the mixture was dried and calcined at 1100 °C and 850 °C for three hours with heating and cooling rates of 5 °C/min, respectively. Then, the calcined powders were weighed according to the formula of 0.95CST–0.05BNT, and the powders were re-milled for six hours by ball milling in water media at the same time. The mixture with PVA solution was pressed into cylinders under a uniaxial pressure of 300 MPa, and sintered at 1275–1350 °C for 20 to 50 minutes by microwave sintering. For a comparison, 0.95CST–0.05BNT ceramics were also prepared at 1275 °C for three hours by conventional sintering. The microwave furnace (MW-L0316V, Changsha Longtech Co. Ltd., Changsha, China) consisted of 2.45-GHz magnetrons with a maximum power of three kW.

The phase constitution was identified by powder X-ray diffraction using $\text{CuK}\alpha$ radiation with a scan width of 10–80° a and scan speed of 10 °/min (XRD; RIGAKU; SmartLab 3; 40kV; 30mA, Beijing, China). The microstructures were observed on the surfaces with scanning electron microscopy (SEM; JEOL, JSM-5900; 15kV, Beijing, China). The sample density was determined by the Archimedes method. The cylinders with a diameter of about 15 mm and thickness of about 7.3 mm were used for evaluating the microwave dielectric properties using a vector network analyzer (Agilent 8722ET) [13,14].

3. Results and Discussion

Figure 1 exhibits the XRD patterns of 0.95CST–0.05BNT ceramics sintered by CS and MWS. We could see that all the samples displayed the characteristic peaks of perovskite-type structures, which could be indexed to be the perovskite structure (ICSD-PDF#81-0562), and no other phase was identified. It showed that different sintering methods had little effect on phase composition.

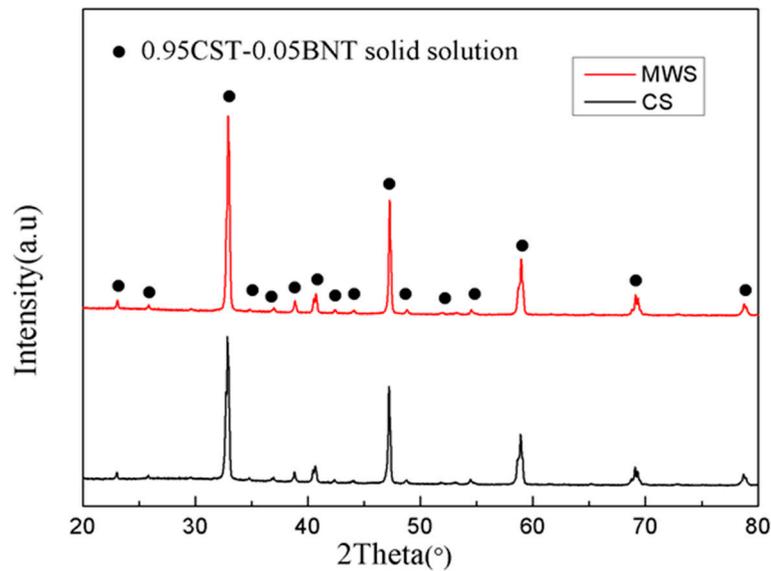


Figure 1. XRD patterns of 0.95CST–0.05BNT samples sintered by different methods.

The SEM micrographs on the surfaces of 0.95CST–0.05BNT samples sintered at 1300 °C for different holding times by MWS are shown in Figure 2a–d. The average grain size increased, and the number of pores reduced gradually as the holding time increased. In order to further compare the difference between MWS and CS ceramics, Figure 2e illustrates the SEM of 0.95CST–0.05BNT samples prepared by conventional sintering at 1275 °C for three hours. It could be seen in Figure 2c, e that there was little change in the grain shape of the MWS samples, but the grain size of the MWS samples (one μm) was smaller than that of the CS samples (three μm). It could be explained that the sintering time was much shorter and the heating rates were much faster in the process of microwaving heating than that of the conventional heating; thus, fine and uniform grains were obtained.

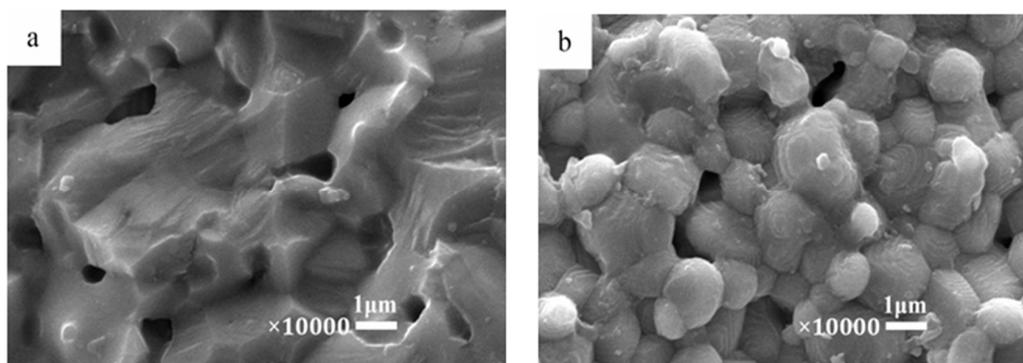


Figure 2. Cont.

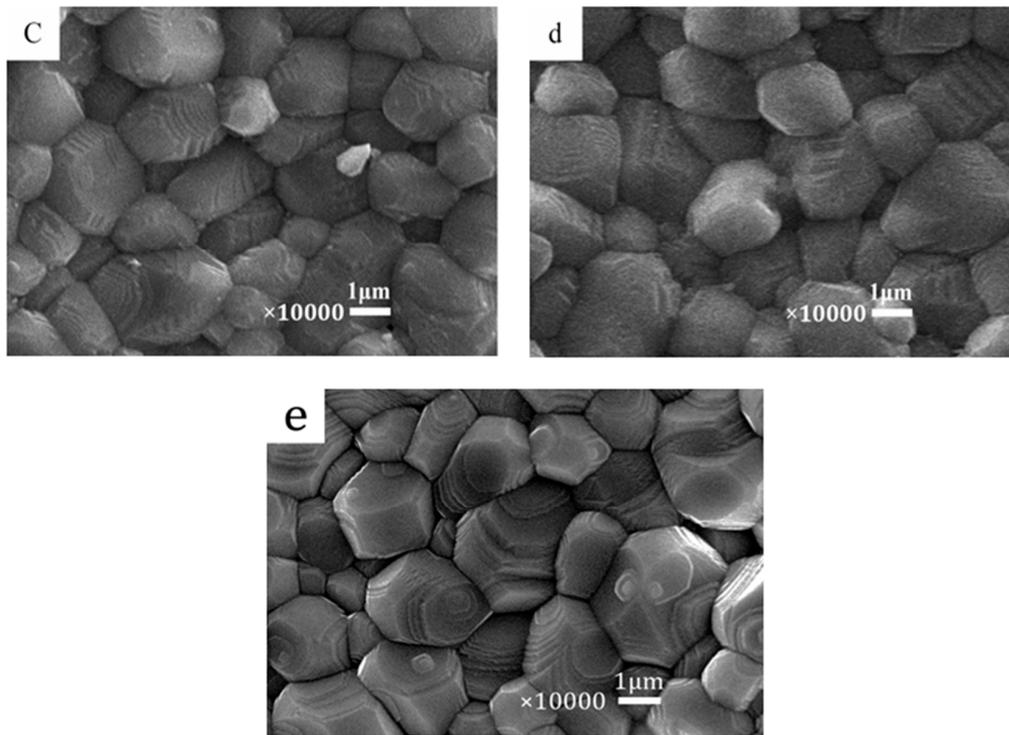


Figure 2. SEM micrographs of 0.95CST–0.05BNT samples sintering at 1300 °C by microwave sintering (MWS), with different holding times: (a) 20 min, (b) 30 min, (c) 40 min, (d) 50 min; (e) 1275 °C hold for three hours by conventional sintering (CS).

The bulk density of 0.95CST–0.05BNT ceramics as a function of different sintering temperatures and holding times is shown in Figure 3. The bulk density increased gradually as the holding time increased. The highest density was obtained when the sintering temperature was 1300 °C for 40 minutes. However, the bulk densities did not increase significantly when the sintering temperature exceeded the optimal value. The grain grew completely in the ultra-high sintering temperature, and the densities of the ceramics were also optimal. All of the samples showed that the optimum bulk densities were obtained when the sintering temperature was 1300 °C for 40 minutes.

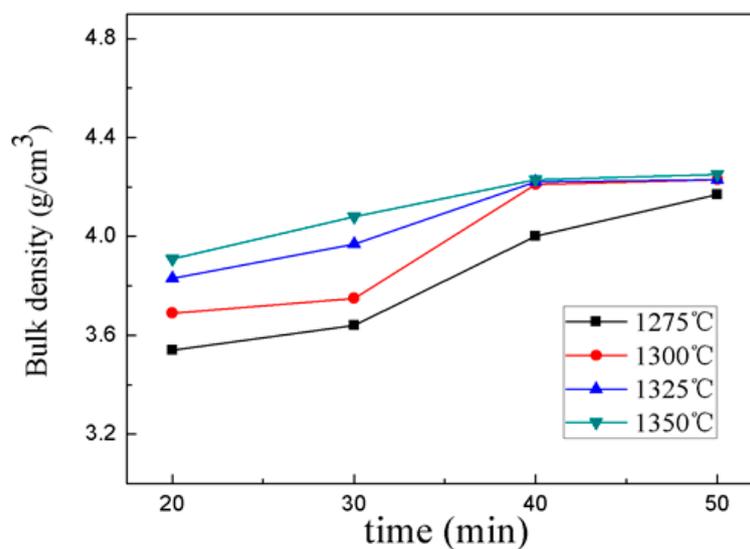


Figure 3. Bulk density of the 0.95CST–0.05BNT samples with different sintering temperatures and holding times by MWS.

Figures 4 and 5 show the dielectric constant (ϵ_r) and quality factor ($Q \times f$) of 0.95CST–0.05BNT samples as functions of different sintering temperatures and holding times. It could be seen from the diagram that the dielectric properties of the samples had been greatly improved with the increased temperature and holding time. The dielectric properties first increased, and then stabilized as the holding time increased. The dielectric constant and quality factor obtained a maximal value when the samples were sintered at above 1300 °C. Considering the sintering and dielectric properties, energy consumption, and other factors, the optimum conditions for the preparation of ceramics by microwave sintering were as follows: the sintering temperature and holding time were 1300 °C and 40 minutes, respectively.

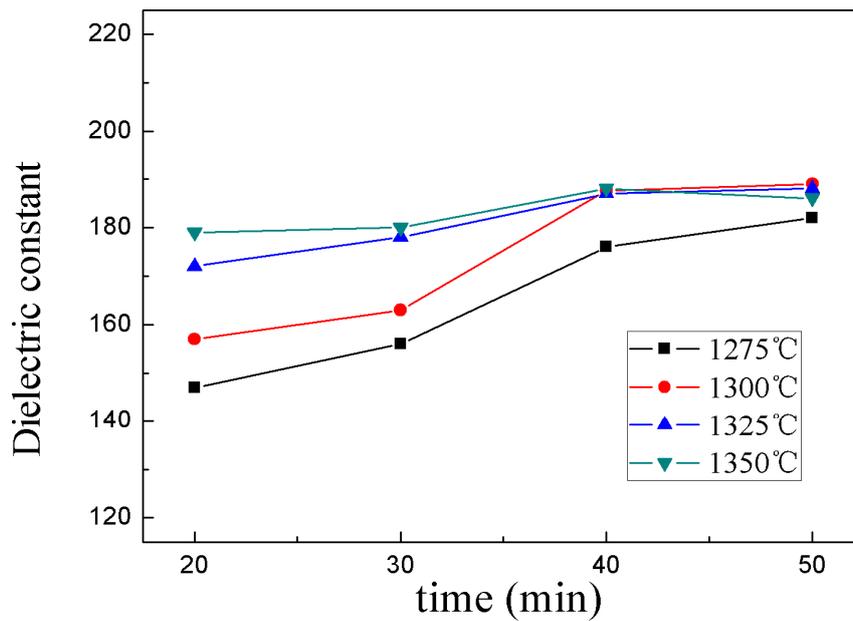


Figure 4. Dielectric constant ϵ_r of the 0.95CST–0.05BNT samples with different sintering temperatures and holding times by MWS.

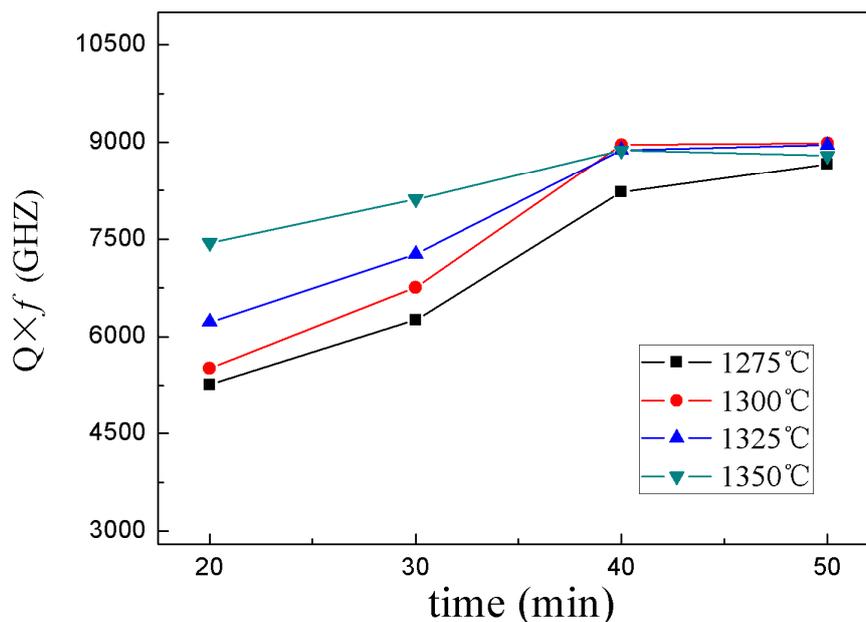


Figure 5. $Q \times f$ value of the 0.95CST–0.05BNT samples with different sintering temperatures and holding times by MWS.

Figure 6 shows the time–temperature curve for 0.95CST–0.05BNT ceramics sintered by MWS and CS. The time required for microwave sintering was much shorter than that of conventional sintering. The sintering period was just about six hours, and the sintering temperature up to 1300 °C only needed 58 minutes by microwave sintering. Moreover, the holding time was only 40 minutes. In contrast, conventional sintering required at least 12.75 hours to reach the highest temperature, and its holding time extended to three h, which led to a sintering period of at least 30 hours.

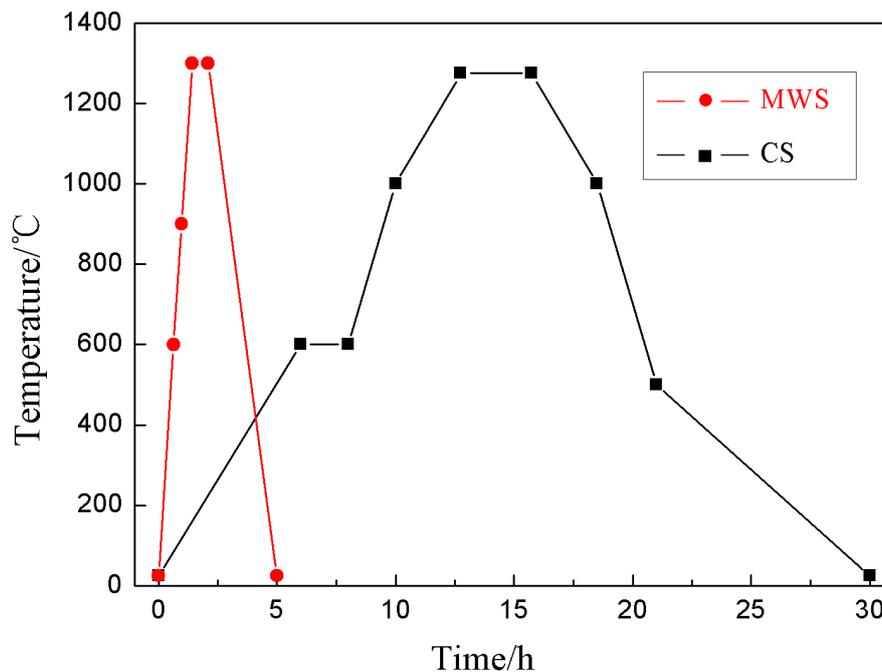


Figure 6. Time–temperature sintering curve for MWS and CS.

Table 1 summarizes the differences between conventional sintering and microwave sintering on the properties of 0.95CST–0.05BNT samples. As we could see, microwave sintering not only shortened the sintering period and holding time, but also improved the properties. The dielectric constant of the MWS samples were higher than those of the CS samples. Overall whole, it was the change of the dielectric constant that was closely consistent with the density of the ceramics. The main cause accounting for the increasing of the dielectric constant was due to the enhancement of the densification. From Table 1, it could be also concluded that the quality factor of the MWS samples was higher than that of the CS samples. This phenomenon was attributed to the more uniform grain size distribution and compact microstructure of the MWS samples. Under microwave radiation, the movement of vacancies and interstitial ions, which parallel the electric field, enhanced instantaneously, which greatly reduced the diffusion barrier, permitting ions to move faster and expediting the grain boundary diffusion and densification rates [15–17]. However, during the conventional sintering, heat was transmitted between objects through conduction, radiation, and convection mechanisms. In addition, conventional sintering led to temperature gradients from the surface to the inside. Therefore, microwave sintering resulted in samples with a more uniform grain size distribution and densification. Besides, the temperature coefficient of resonance frequency (τ_f) of the MWS samples was also closer to zero, which decreased greatly from +639 to $+520 \times 10^{-6} / ^\circ\text{C}$.

Table 1. Microwave properties of 0.95CST–0.05BNT samples prepared with different sintering processes.

Parameters	MWS (CST-BNT)	CS (CST-BNT)
Sintering period (h)	6	30
Holding time (h)	0.67	3
Sintering temperature (°C)	1300	1275
Bulk densities (g/cm ³)	4.23	4.22
Dielectric constant	187.6	185.5
Quality factor (GHz)	8958	8116
$\tau_f (\times 10^{-6} / ^\circ\text{C})$	+520	+639

4. Conclusions

The 0.95CST–0.05BNT samples had been prepared successfully by microwave sintering. The sintering period only needed six hours by microwave sintering; thus, this method could greatly improve production efficiency. Moreover, the 0.95CST–0.05BNT ceramics showed more uniform grain size distribution, and microwave sintering greatly shortened the sintering period and holding time. As a result, the optimal microwave dielectric properties with a dielectric constant of 187.6, $Q \times f$ value of 8958 GHz, and temperature coefficient of resonant frequency of $+520 \times 10^{-6} / ^\circ\text{C}$ were achieved at 1300 °C for 40 minutes by microwave sintering. In particular, the temperature coefficient of resonance frequency (τ_f) of MWS ceramics was also closer to zero, which decreased greatly from +639 to $+520 \times 10^{-6} / ^\circ\text{C}$.

Author Contributions: L.T. and C.Y.S. conceived and designed the experiments; L.T. performed the experiments; L.T. and J.N. analyzed the data; H.W. contributed reagents/materials/analysis tools; L.T. wrote the paper.

Acknowledgments: This work was supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT), IRT1146.

Conflicts of Interest: The authors declare no conflict of interest.

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