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Ceramics International 39 (2013) S335–S339

CERAMICS INTERNATIONAL

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Dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramics prepared by microwave sintering

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Available online 27 October 2012

Abstract

A comparative study on the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ($x=0.1$–0.6) ceramics prepared by microwave sintering (MS) and conventional sintering (CS) has been done. It was found that MS samples need lower temperature and much shorter time than CS samples to obtain the same degree of densification. Compared with CS samples, MS samples possessed smaller grain size, better densification and more uniform grain growth. The dielectric properties of the samples were measured as a function of temperature. It was observed that the dielectric constant was higher for MS samples compared with that of CS samples especially in the ferroelectric phase.

Keywords: A. Microwave processing; C. Dielectric properties; Barium strontium titanate

1. Introduction

Barium strontium titanate (BST), $Ba_{1-x}Sr_xTiO_3$ is a perovskite-structured ferroelectric material, and it is a solid solution composed of barium titanate and strontium titanate. For its favorable dielectric and ferroelectric properties such as high dielectric constant, alterable Curie temperature, low dielectric loss and high tunability of dielectric behavior, it has been widely used in preparation of dynamic random access memories (DRAM), dielectric capacitors, microwave phase shifters, transducers, positive temperature coefficient resistors (PTC) [1–4].

Many efforts have been put to improve the microstructure and electrical properties of BST ceramics synthesized by conventional and other chemical processes [5–7]. However, very limited literature reported is available on the microwave sintering of BST ceramics, especially for a wide range of Ba/Sr ratio [8–11].

Microwave sintering is a unique technique alternative to the conventional sintering. This technique requires less time and lower temperature to achieve the same quality with ceramics as sintered by conventional route. Furthermore smaller grain sizes and more uniform microstructure can be developed by microwave sintering [8], by which the heat is generated internally within the material through microwave–material interaction instead of originating from external sources [9]. Microwave sintering heated rapidly as the material is heated by energy conversion rather than through energy transfer, and it is very uniform as the microwave–material interaction occurred from the inside to the outside simultaneously rather than energy transfer from the outside to the inside.

Here we report our results on microstructure and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ($x=0.1$–0.6) ceramics sintered by microwave and conventional methods.

2. Experimental

$Ba_{1-x}Sr_xTiO_3$ ($x=0.1$–0.6, denoted as BST10, BST20 for $x=0.1$, $0.2\ldots$) powders were synthesized by the conventional solid-state reaction of barium titanate ($BaTiO_3$, 99.9%) and strontium titanate ($SrTiO_3$, 99.9%) powders. Stoichiometric mixtures of the raw powders were mixed in ethanol medium with zirconia balls and ball-milled for 24 h. After drying, the mixtures were calcined at temperatures ranged 1100 °C to 1200 °C for 2 h, and remilled for 24 h to reduce the particle size for sintering, and then granulated with polyvinyl alcohol (PVA) which is used as a

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http://dx.doi.org/10.1016/j.ceramint.2012.10.089

Table 1
Detailed sintering temperature.

Component	Microwave sintering (°C)	Conventional sintering (°C)
BST60	1300	1320
BST50	1280	1300
BST40	1280	1300
BST30	1260	1280
BST20	1260	1280
BST10	1220	1240

binder. The granulated powders were pressed into discs in diameter of 10 mm and thickness of 1.0 mm.

Jae-Ho Jeon has reported the effect of sintering temperature on microstructure and dielectric constant of $Ba_{1-x}Sr_xTiO_3$ [12]. In this paper, we select a suitable temperature for each component and each sintering method instead of a same temperature. For conventional sintering, one set of these pellets were sintered at temperatures ranged 1240 °C to 1320 °C for 4 h, maintaining 3 °C/min heating rate. Another set of pellets were sintered by a microwave furnace (2.45 GHz, 1.4 kW) at temperatures ranged 1220 °C to 1300 °C for only 0.5 h of soaking time. The heating rate was maintained at 30 °C/min (by controlling the input power). The detailed sintering temperature is listed in Table 1.

For electrical characterization, the ceramic pellets were polished, coated with silver paste, and fired at 600 °C for 10 min.

Their microstructure morphology was obtained by scanning electron microscopy (SEM, JSM EMP-800, JEOL, Japan), and phase structure was analyzed by an X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with CuKα radiation. The temperature-dependence of dielectric properties was investigated with an LCR meter (HP4284A, Agilent, Palo Alto, CA). The polarization–electric field hysteresis loops were measured with a ferroelectric analyzer (Premier II, Radiant, USA).

3. Results and discussion

The XRD patterns of the conventional and microwave synthesized samples are shown in Fig. 1. This confirms the formation of a single phase perovskite BST structure. As Sr content increases, the diffraction peaks move toward high-angle direction, and the phase structure undergoes a transition from tetragonal (BST10, BST20, BST30) to cubic (BST40, BST50, BST60) gradually. MS samples achieve the same intensity of peak (110) as CS samples, which indicates that they have the same crystallization.

The surface microstructure of the MS and CS samples are shown in Fig. 2 and the grain sizes are listed in Table 2. Compared with CS samples, MS samples show smaller grain size, better densification and more uniform grain growth as shown in SEM images. The rapidity and

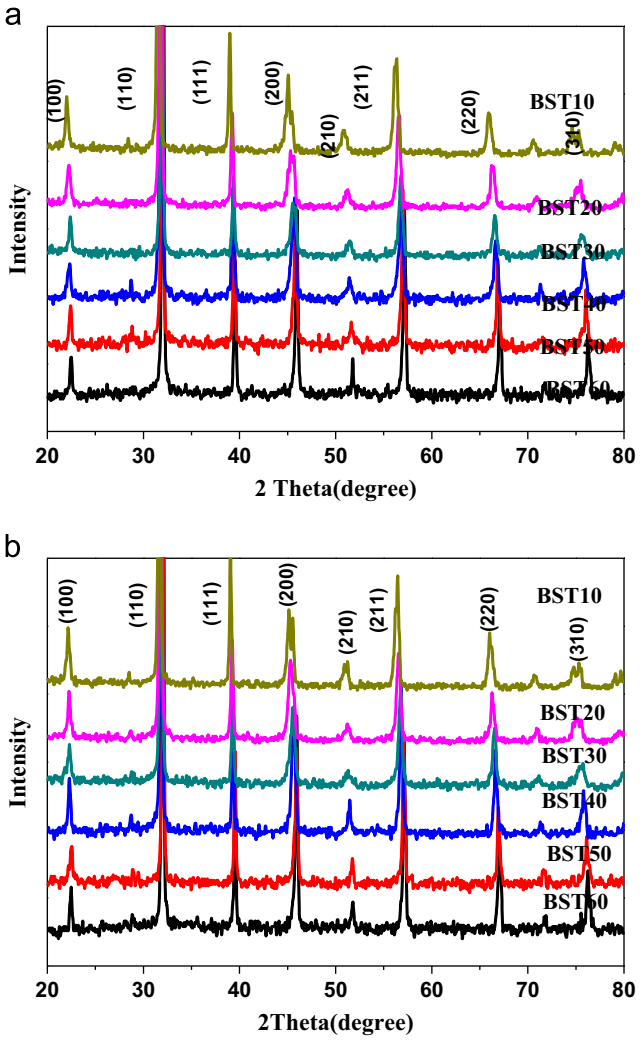

Fig. 1. XRD patterns of BST ceramics: (a) MS samples and (b) CS samples.

uniformity of microwave sintering avoids undesirable grain growth and provides a finer and more uniform microstructure.

Temperature dependence of relative dielectric constant and dielectric loss of MS and CS samples are shown in Fig. 3, and dielectric parameters are summarized in Table 3. Compared with the CS samples, MS samples possess a higher maximum dielectric constant ε_m for they have smaller grain size, which agrees with those reported elsewhere [11]. For BST10, BST20, BST30 and BST40, the Curie temperature of samples sintered by the microwave method was higher than those sintered by the conventional method, and the effect was opposite for BST50 and BST60. Compared with the CS samples, the dielectric constant (25 °C, 10 kHz) of MS samples increased about 20%, 35%, 25%, 9.2%, 2.0% and 1.5% for BST10, BST20, BST30, BST40, BST50 and BST60, respectively. BST ceramics were in the ferroelectric phase at room temperature (25 °C) when $x \leq 0.35$ [13], it was observed that the dielectric constant was higher for MS samples

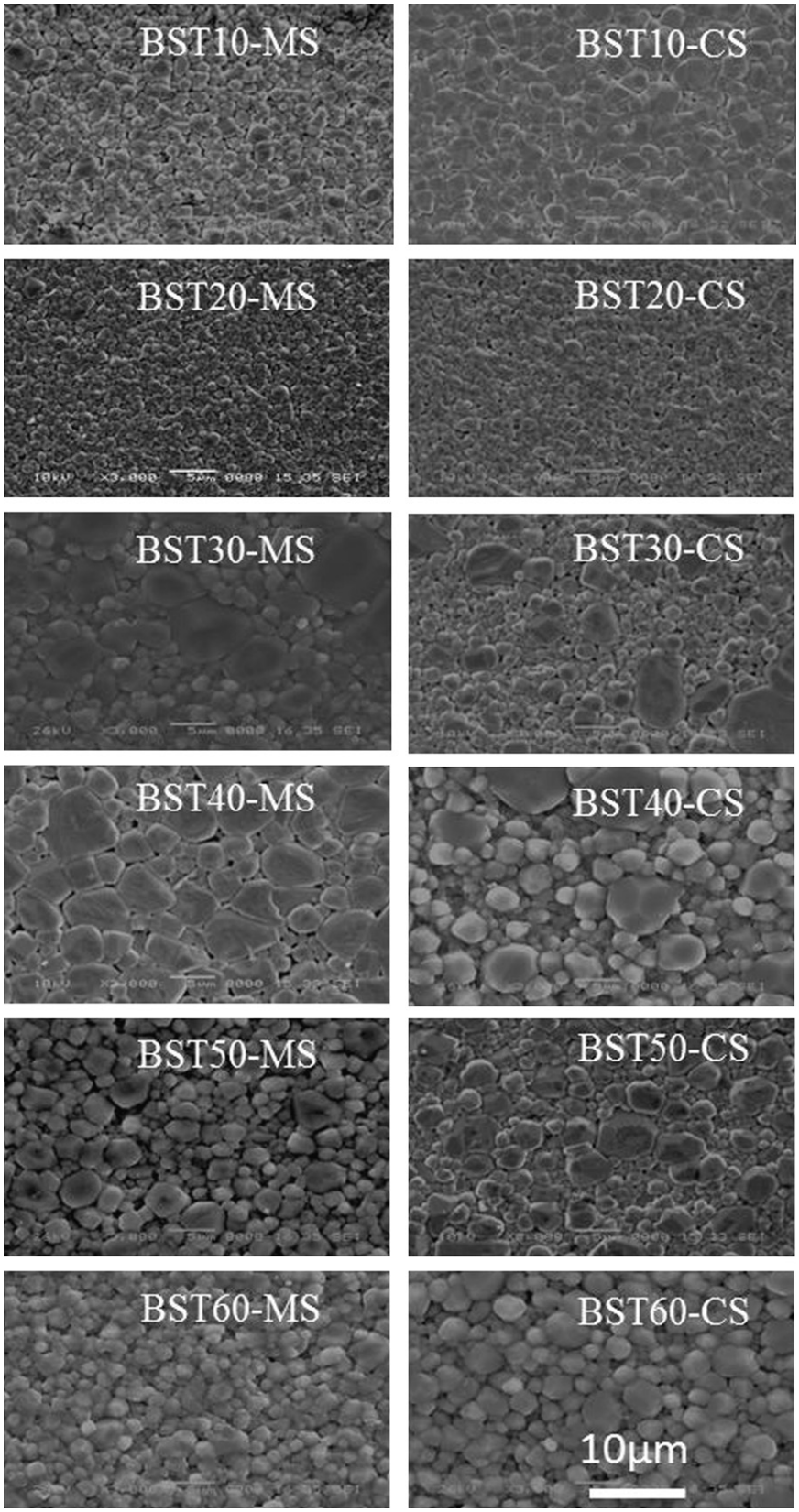

Fig. 2. SEM microstructure picture of MS samples and CS samples.

Table 2
Grain sizes of BST ceramics.

Ceramic samples	Grain size-MS (μm)	Grain size-CS (μm)
BST10	1.4	2.1
BST20	0.9	1.3
BST30	2.4	2.7
BST40	2.9	2.7
BST50	2.2	2.4
BST60	1.7	2.1

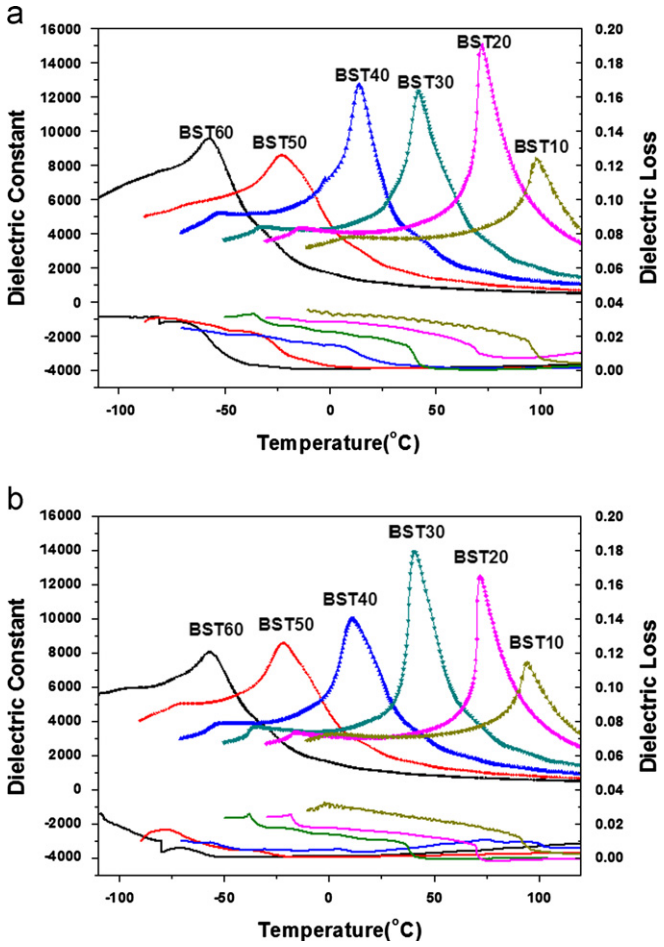

Fig. 3. Temperature dependence of relative dielectric constant and dielectric loss at 10 kHz: (a) MS samples and (b) CS samples.

Table 3
Dielectric parameters of MS samples and CS samples (10 kHz).

Ceramic samples		T_c	ε_m	ε_r (25 °C)	tan δ (25 °C)
MS	BST10	98.0	8353	3736	0.0315
	BST20	71.7	15,035	4130	0.0258
	BST30	42.4	12,342	5452	0.0181
	BST40	14.3	12,727	7263	0.0046
	BST50	−22.6	8572	2193	0.0007
	BST60	−57.4	9533	1096	0.0007
CS	BST10	93.7	7416	3102	0.0267
	BST20	71.6	12,480	3061	0.0151
	BST30	40.3	13,960	4353	0.0103
	BST40	11.1	10,018	6652	0.0039
	BST50	−21.8	8569	2151	0.0007
	BST60	−56.6	8038	1080	0.0013

than that of CS samples especially in the ferroelectric phase. This is due to the smaller grain size, better densification and more uniform grain growth. However, the dielectric loss of MS samples was almost the same as the CS samples.

The polarization versus electric field (P vs. E) behavior was measured using an ac field of 60 kV/cm at 10 Hz. P–E loops for BST10, BST20 and BST30 sintered by microwave and conventional methods are shown in Fig. 4. There is no obvious difference in the coercive field (Ec) and remnant polarization (Pr) between MS samples and CS samples. Detailed analyses should be studied further.

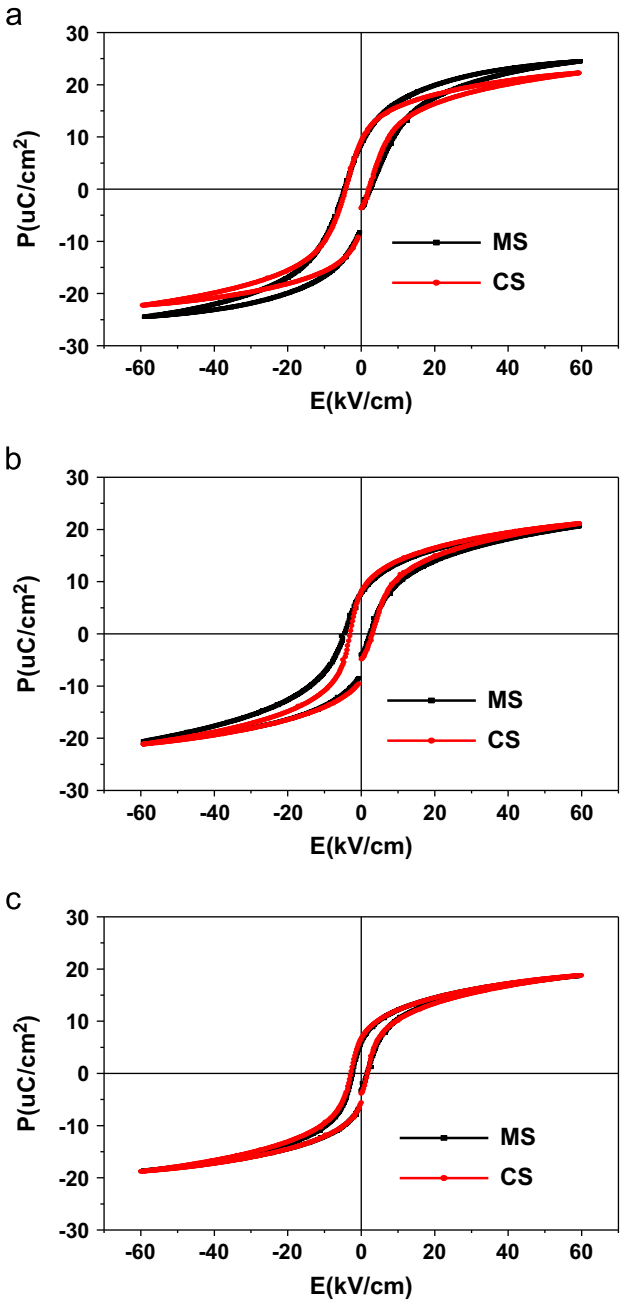

Fig. 4. P–E loops of MS samples and CS samples: (a) BST10; (b) BST20 and (c) BST30.

4. Conclusions

Microwave sintering greatly reduces the time and energy required to sintering process. It also has significant effects on microstructure and dielectric properties of ceramics. From the study of BST ($x=0.1$–0.6) ceramics prepared by microwave sintering and conventional sintering, it is seen that MS samples possessed smaller grain size, better densification and more uniform grain growth. The dielectric properties of the samples were measured as a function of temperature, implying that MS samples have higher maximum dielectric constant, higher dielectric constant at room temperature especially in the ferroelectric phase. There is no obvious difference in dielectric loss and *P*–*E* loops.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Nos. 51072136 and 50932007).

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