

# Structural and dielectric properties of $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ceramics

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**Abstract** The  $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$  (BSTS) ceramics were prepared by conventional ceramic method. The crystalline structure and morphology were studied by X-ray diffraction and scanning electron microscopy, respectively. The dielectric constant and loss as a function of temperature and external bias electric field were investigated. Experimental results show that with the increasing of sintering temperature, the peak permittivity increases dramatically and  $\tan\delta$  increases at ferroelectric state while does not change apparently at paraelectric state. With the increasing of the  $\text{Sn}^{4+}$  concentration in the BSTS structure, the Curie temperature decreases.

**Keywords**  $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{1-y}\text{Sn}_y\text{O}_3$  ceramics · Solid-state reaction · Dielectric properties

## 1 Introduction

Many experimental and theoretical studies have been performed on the dielectric properties of barium titanate. The Curie temperature of  $\text{BaTiO}_3$  is about 120 °C. Thus the application of  $\text{BaTiO}_3$  ceramics at room temperature is limited for its high  $T_c$ . However, the structural and electrical properties can be modified via partial substitution of either Ba-ions (A-site doping) or Ti-ions (B-site doping) which make the cubic structure more stable relative to the tetragonal structure than in pure  $\text{BaTiO}_3$  [1].

The structure and dielectric properties of barium strontium titanate system (by substituting Ba ions at the A-site of

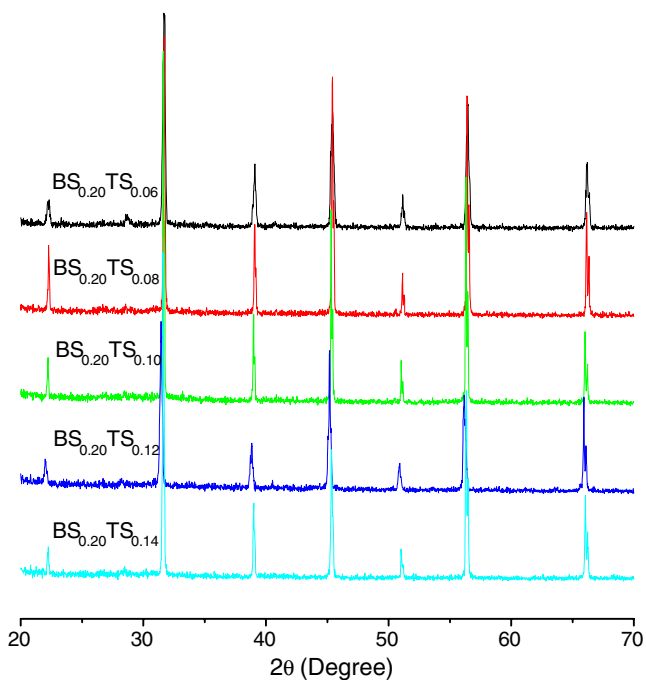
$\text{BaTiO}_3$  with Sr) and barium titanate stannate system (by substituting Ti ions at the B-site of  $\text{BaTiO}_3$  with Sn) have been widely studied by many researchers [2–8]. However, little work has been reported on BSTS that is obtained by substituting ions at the A-site and B-site of the  $\text{BaTiO}_3$  simultaneously with Sr and Sn in the perovskite structure  $\text{ABO}_3$ . The present paper reports on the  $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$  (BSTS) by solid-state reaction for different concentrations of Sn. The dielectric properties as a function of temperature and external bias electric field were studied.

## 2 Experimental procedure

The  $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$  ( $\text{BS}_{0.2}\text{TS}_x$ ,  $x=0.06, 0.08, 0.10, 0.12, 0.14$ ) were prepared by conventional ceramic method with high-purity  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaCO}_3$  and  $\text{SnO}_2$ . Stoichiometric composition of the chemicals was thoroughly mixed in distilled water by ball milling with zirconia balls for 12 h. The mixture was dried granulated and calcined at 1050 °C for 3 h, then crushed and ball-milled again for 24 h to obtain fine powders. The calcined powders were mixed with 8 wt.% of polyvinyl alcohol solution and then pressed into disc-shaped pellets with a diameter of 10 mm. The green pellets were sintered in air at 1150, 1200, 1250, 1300, 1350 °C for 2 h. Heating rate was kept at 3 °C/min.

The structure of the samples was analyzed by X-ray diffraction method using BRUCKER D8 powder diffractometer using  $\text{CuK}\alpha$  radiation in a range of  $20^\circ \leq 2\theta \leq 70^\circ$ . The microstructure and the grain size were investigated by scanning electronic microscopy (SEM, JSM EMP-800). For dielectric property study, ceramic disks were polished and electroded with silver paste by painting onto the surface and then fired at 520 °C for 20 min. The dielectric constant

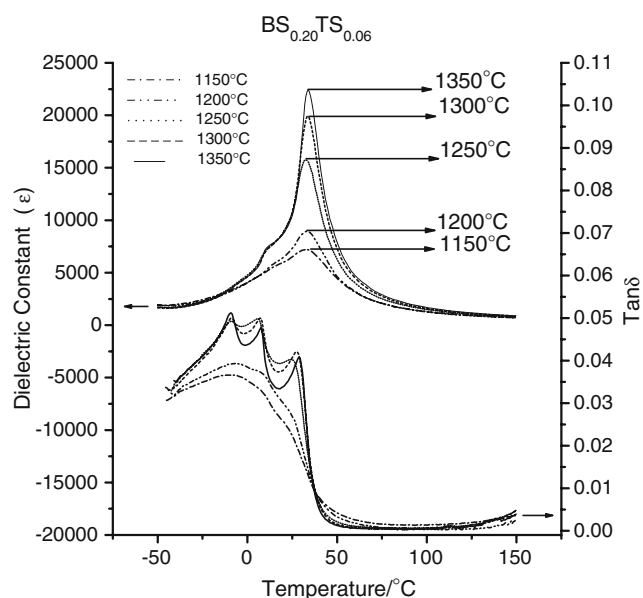
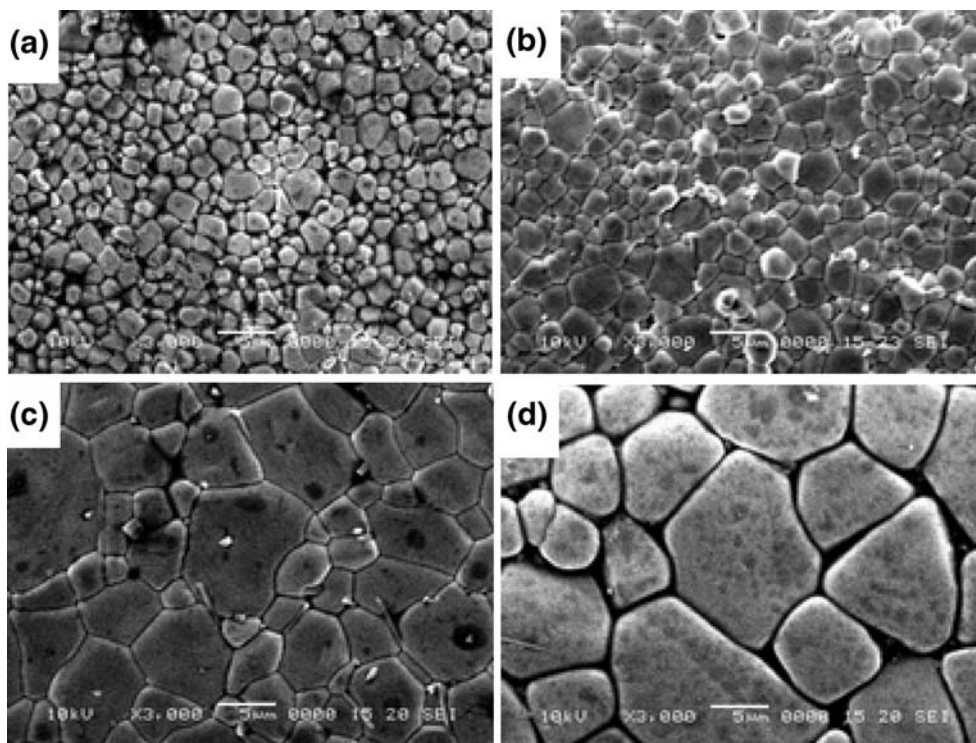
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**Fig. 1** XRD patterns of  $BS_{0.20}TS_x$  ceramics

and loss of the samples were measured in the temperature range of  $-50$  to  $150$  °C using a HP 4284A LCR meter. The dielectric constant and loss were also measured under external biased electric field using Th2816 LCR meter. The direct current (dc) electric field was applied on the polished disks with a thickness of  $0.3$  mm by a Keithley Model 6517 Electrometer.

**Fig. 2** SEM photographs of  $BS_{0.20}TS_{0.06}$  samples sintered at (a)  $1150$  °C, (b)  $1200$  °C, (c)  $1250$  °C, (d)  $1350$  °C for 2 h



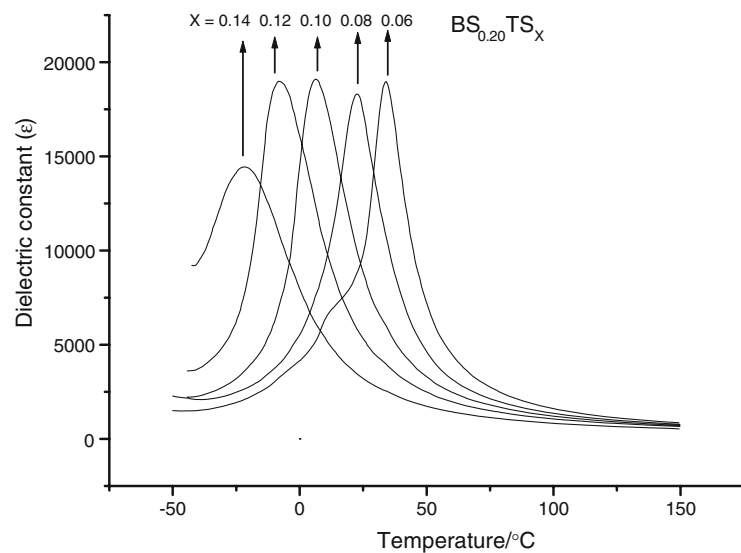
**Fig. 3** Temperature dependence of the dielectric constant and  $\tan\delta$  (at 1 kHz) for  $BS_{0.20}TS_{0.06}$  samples sintered at different temperature

### 3 Results and discussion

The X-ray diffraction pattern of the  $BS_{0.2}TS_x$  ceramics sintered at  $1300$  °C for 2 h are shown in Fig. 1. The diffraction patterns indicate that the samples are perovskite structure without any secondary phase.

Figure 2 shows SEM images of the  $BS_{0.20}TS_{0.06}$  ceramics sintered at various temperatures from  $1150$  to

**Fig. 4** Temperature dependence of dielectric constant for  $BS_{0.20}TS_x$  with different Sn content



sample	Sn <sup>4+</sup> content (%)	T <sub>c</sub> (°C)	Rate of T <sub>c</sub> shifting (°C/mol%)		ε <sub>r</sub> <sup>peak</sup>
BS <sub>0.20</sub> TS <sub>0.06</sub>	6	34.1		6.9	18980
BS <sub>0.20</sub> TS <sub>0.08</sub>	8	22.5	5.8		18321
BS <sub>0.20</sub> TS <sub>0.10</sub>	10	6.4	8.0		19103
BS <sub>0.20</sub> TS <sub>0.12</sub>	12	-8.2	7.3		18981
BS <sub>0.20</sub> TS <sub>0.14</sub>	14	-21.4	6.6		14442

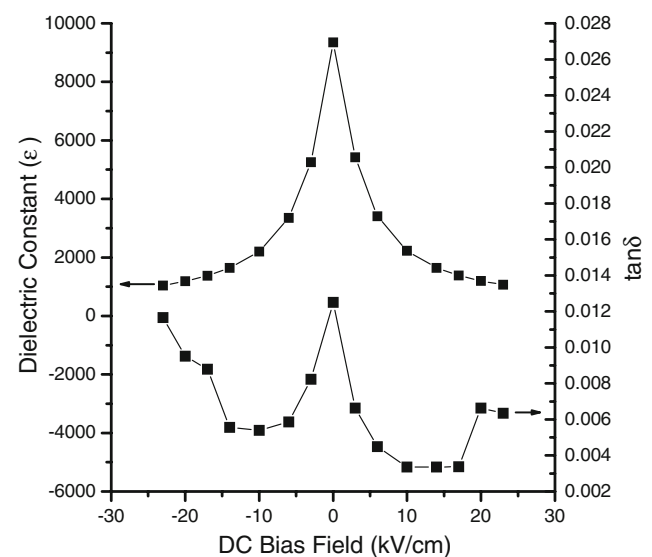
1350 °C. With the increasing of sintering temperature, the grain size increases dramatically.

The variation of dielectric constant with sintering temperature for the  $BS_{0.20}TS_{0.06}$  ceramic is shown in Fig. 3. An obvious feature is that the peak permittivity decreases and its temperature spectrum broadens with the decreasing of sintering temperature. When the sintering temperature increases from 1150 to 1350 °C, the peak permittivity increases from 7,200 to 22,428. That is because the grain size increases largely with the increasing of sintering temperature as shown in Fig. 2. Another feature of the dielectric behavior is that with the increasing of

sintering temperature,  $\tan\delta$  increases at the ferroelectric state, while does not change obviously at paraelectric state. Furthermore,  $\tan\delta$  is much lower in the paraelectric state ( $\sim 0.001$ ) than in the ferroelectric state ( $\sim 0.04$ ), owing to the disappearance of domain [9].

**Table 1** Dielectric property of  $BS_{0.20}TS_x$  (samples sintered at 1300 °C for 2 h).

Sample	Sn <sup>4+</sup> content (%)	T <sub>c</sub> (°C)	Rate of T <sub>c</sub> shifting (°C/mol%)		ε <sub>r</sub> <sup>peak</sup>
BS <sub>0.20</sub> TS <sub>0.06</sub>	6	34.1		6.9	18,980
BS <sub>0.20</sub> TS <sub>0.08</sub>	8	22.5	5.8		18,321
BS <sub>0.20</sub> TS <sub>0.10</sub>	10	6.4	8.0		19,103
BS <sub>0.20</sub> TS <sub>0.12</sub>	12	-8.2	7.3		18,981
BS <sub>0.20</sub> TS <sub>0.14</sub>	14	-21.4	6.6		14,442



**Fig. 5**  $\epsilon$ -E characteristics of BS20TS6-1300 ceramic at room temperature (100 kHz)

Figure 4 shows the temperature dependence of dielectric constant for  $\text{BS}_{0.20}\text{TS}_x$  with different Sn content sintered at 1300 °C for 2 h. First, we can see a clear Curie peak for all the curves, due to the phase transition from cubic to tetragonal phase. When the temperature is above the Curie point, the thermal energy of the crystal lattice is high enough to make all equilibrium positions of the titanium ion equally, and the cubic symmetry will be stabilized for all cells. When the temperature is below the Curie temperature, the thermal energy is no longer enough to overcome the electric forces of interaction between separate cells with displaced titanium and oxygen ions (such cells obviously acquire electrical polar moment and become dipoles). The material transforms into spontaneous polarization. The displacement of titanium and oxygen slightly distorts the shape of cell. The axis along which displacement takes place elongated and the other two axes shortened, and the cubic crystalline structure turns into tetragonal. Thus, a phase transition takes place when the temperature passes through the Curie point [10]. Second, another unobvious peak can only be observed from the curve of  $\text{BS}_{0.20}\text{TS}_{0.06}$  ceramics, due to the phase transition from the tetragonal to trigonal phase. With the increasing of  $\text{Sn}^{4+}$  concentration, the overlap of two phase transition (cubic–tetragonal, tetragonal–trigonal) into one can be observed and the diffuseness of this transition increases. The samples with higher content of  $\text{Sn}^{4+}$  exhibit more gentle slope of permittivity to temperature. It can be regarded as a result that the barium stannate is a non-ferroelectric component [7, 10]. Third, from all these curves, we can see that the Curie temperature is shifted to lower temperature as the amount of tin increases. In the  $\text{BaTiO}_3$  structure, the  $\text{Ba}^{2+}$  (~1.34 Å) is replaced by smaller  $\text{Sr}^{2+}$  (~1.27 Å) and  $\text{Ti}^{4+}$  (~0.76 Å) is replaced with larger  $\text{Sn}^{4+}$  (~0.93 Å). As a result, the observations can be explained in terms of the decrease in polarizability due to more tightening of the bond between the  $\text{Sn}^{4+}$  and the  $\text{O}^{2-}$  ions [1]. Experimental data show that the Curie temperature decreases at an average rate of 6.9 K/mol% as the amount of  $\text{Sn}^{4+}$  increases. The Curie temperature of  $\text{BS}_{0.20}\text{TS}_x$  ceramics is listed in the Table 1, and together with the value of permittivity at the Curie point.

The effect of dc bias on the dielectric constant and loss of the BSTS was studied by varying applied dc field. The typical dc field dependence of the dielectric constant and  $\tan\delta$  for the composition  $\text{BS}_{0.20}\text{TS}_{0.06}$  ceramics sintered at 1300 °C for 2 h at 100 kHz is shown in Fig. 5. When applying a dc field, the dielectric constant reduces strongly. The tunability ( $k$ ) is defined as the percentage change of the

dielectric constant under a specific dc bias. It is calculated by using the expression:

$$k = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \times 100\% \quad (1)$$

where  $\varepsilon(0)$  and  $\varepsilon(E)$  represent the dielectric constant at zero and a certain E field, respectively. The tunability measurements were taken with an applied electric field that range from 0 to  $\pm 23$  kV/cm at 100 kHz. The tunability of  $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{0.94}\text{Sn}_{0.06}\text{O}_3$  under sintering condition of 1300 °C for 2 h is the largest and reaches about 88.6% at applied electric field of 23 kV/cm. The values of  $\tan\delta$  at 100 kHz range from 0.0122 at zero bias to 0.0074 at 23 kV/cm.

#### 4 Conclusion

The  $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$  ceramics were prepared by conventional solid-state reaction. The BSTS ceramics are single perovskite phase. As the sintering temperature decreases, the peak permittivity decreases and its temperature spectrum broadens while the dielectric loss decreases within the ferroelectric state but does not change obviously at paraelectric state. With the increasing of  $\text{Sn}^{4+}$  concentration, the two phase transitions (cubic–tetragonal, tetragonal–trigonal) overlap into one and the diffuseness of this transition increases. Experimental data show that the Curie temperature decreases at an average rate of 6.9 K/mol% as the amount of  $\text{Sn}^{4+}$  increases. The maximum tunability of 88.6% at applied electric field of 23 kV/cm is achieved from  $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{0.94}\text{Sn}_{0.06}\text{O}_3$  under sintering condition of 1300 °C for 2 h.

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#### References

1. K.H. Yoon, J.H. Kim, K.H. Jo, *J. Mater. Sci.* **23**, 61–64 (1988)
2. W. Liou, B.S. Chiou, *Mater. Chem. Phys.* **51**, 59–63 (1997)
3. J. Zhai, X. Yao, H. Chen, *Ceram. Int.* **30**, 1237–1240 (2004)
4. R. Varatharajan, S. Madeswaran, R. Jayavel, *J. Cryst. Growth* **225**, 484–488 (2001)
5. L. Radhapiyari, O.P. Thakur, C. Prakash, *Mater. Lett.* **57**, 1824–1829 (2003)
6. H.V. Alexandra, C. Berbecaru, A. Ioachim, *Mater. Sci. Eng. B* **109**, 152–159 (2004)
7. W. Smiga, *Ferroelectrics* **192**, 345–347 (1997)
8. C. Kajtoh, *Ferroelectrics* **192**, 335–337 (1997)
9. B. Zhang, X. Yao, L. Zhang, J. Zhai, *Ceram. Int.* **30**, 1773–1776 (2004)
10. B. Tareev, *Physics of Dielectric Materials* (Mir, Moscow, 1975), pp. 203–212