JOURNAL OF MATERIALS SCIENCE **37** (2002) 3739–3745

Direct-current field dependence of dielectric properties in B_2O_3-SiO_2 glass doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics

ZHAI JIWEI*
Functional Materials Research Laboratory, Tongji University, Shanghai 200092, Peoples' Republic of China; Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, Peoples' Republic of China
E-mail: apzhai@cityu.edu.hk

YAO XI, CHENG XIAOGANG, ZHANG LIANGYING
Functional Materials Research Laboratory, Tongji University, Shanghai 200092, Peoples' Republic of China

HAYDN CHEN
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, Peoples' Republic of China

The $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics doped B_2O_3-SiO_2 glass prepared by a sol-gel process and the effect of glass content on the DC field dependence of dielectric characteristics in $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics were studied. The samples were observed and analysed by SEM and X-ray diffraction. The dielectric constant of a BST sample with 1 mol% B_2O_3-SiO_2 sintered at 1250°C was as good as that of undoped BST sintered at 1340°C. The dielectric constant samples decreases as the applied DC field increases. The influence of the DC field on the loss factor is much less than that on the dielectric constant. With increasing of the applied voltage, the T_c was increased and the peaks were surpressed and broadened. With increasing of glass content, the peaks were also surpressed and broadened. The maximum dielectric constant and the percentage change of dielectric constant under a DC field increase. © *2002 Kluwer Academic Publishers*

1. Introduction

The dielectric constant of barium strontium titanate (BST) can be varied by an applied direct current electric field, and this has led to their use as variable elements in tunable microwave devices. Such devices include phase shifters, tunable filters, steerable antennas, etc. [1–5]. The Curie temperature of BST can be controlled to meet the requirements of various applications by varying the strontium molar fraction and the dielectric properties of BST can also be optimized for a particular operating temperature between 30 and 400 K by varying the strontium molar fraction.

(Ba, Sr) TiO_3 has a sintering temperature of ∼1400°C [6]. When materials are sintered at such high temperature, the bottom electrode (for thick film or thin film technology) or inner electrode (for MLC structure) must be of a noble metal, such as Pt electrode, which increases manufacturing costs. Therefore, studies of (Ba, Sr)TiO_3 ceramics have focused on decreasing the sintering temperature and improving the dielectric properties by controlling the sintering conditions and microstructure and by adding sintering aids [7–9]. One method of decreasing the sintering temperature is to add sintering aids that have low melting points and make liquid phases below the sintering temperature [7, 10]. The reaction between the sintering aids and the ceramics cause the formation of a secondary phase with a low dielectric constant. Some sintering aids improve dielectric properties because they incorporate into the grain and restrain the formation of a secondary phase. In general, low-temperature sintering degrades dielectric properties, because the dielectric constants of the sintering aids are lower than that of the ceramics. However, no report on the DC field dependence of dielectric properties has been conducted.

The purpose of this study is to investigate how B_2O_3-SiO_2 glass doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics affects the dielectric properties and to understand the DC field dependence of dielectric constant and dielectric loss.

2. Experimental

The precursor solution used to prepare BSBS powder was barium acetate $Ba(CH_3COO)_3$ (purity ≥ 99%, Shanghai Chemical Reagent Co.), strontium acetate $Sr(CH_3COO)_3 \cdot 1/2H_2O$ (purity ≥ 99.5%, Shanghai

---

*Author to whom all correspondence should be addressed.

TABLE I Sintered condition, composition, relative density and porosity for all samples

Sample	$Ba_{0.6}Sr_{0.4}TiO_3$ (mol%)	Doped (mol%) B_2O_3	Doped (mol%) SiO_2	Sintering temperature	ρ_{rel} (%)	Porosity (%)
BSTS0	100	0	0	1340°C, 2 h	95.2	2.1
BSTS1	99	0.25	0.75	1250°C, 2 h	98.4	1.2
BSTS2	95	1.25	3.75	1150°C, 2 h	89.6	9.8
BSTS3	90	2.5	7.5	1125°C, 2 h	93.7	6.1
BSTS4	80	5.0	15.0	1125°C, 2 h	95.8	3.2

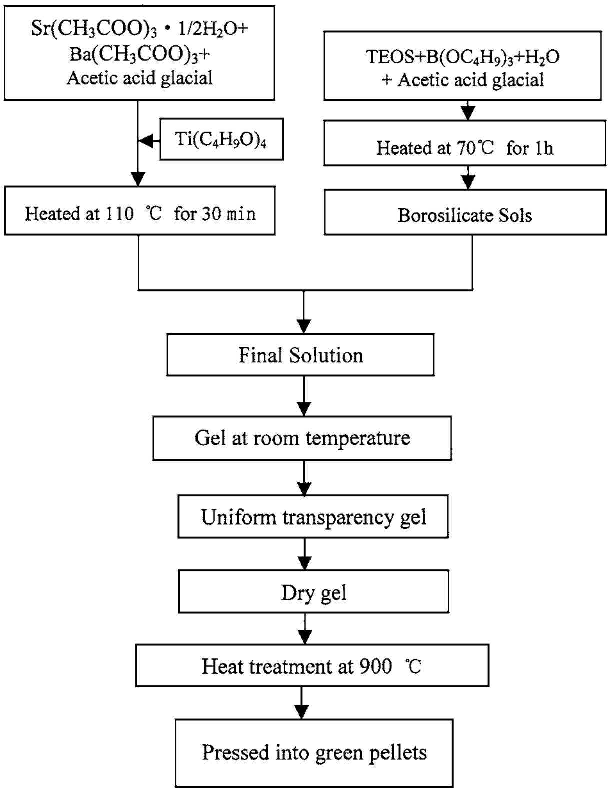
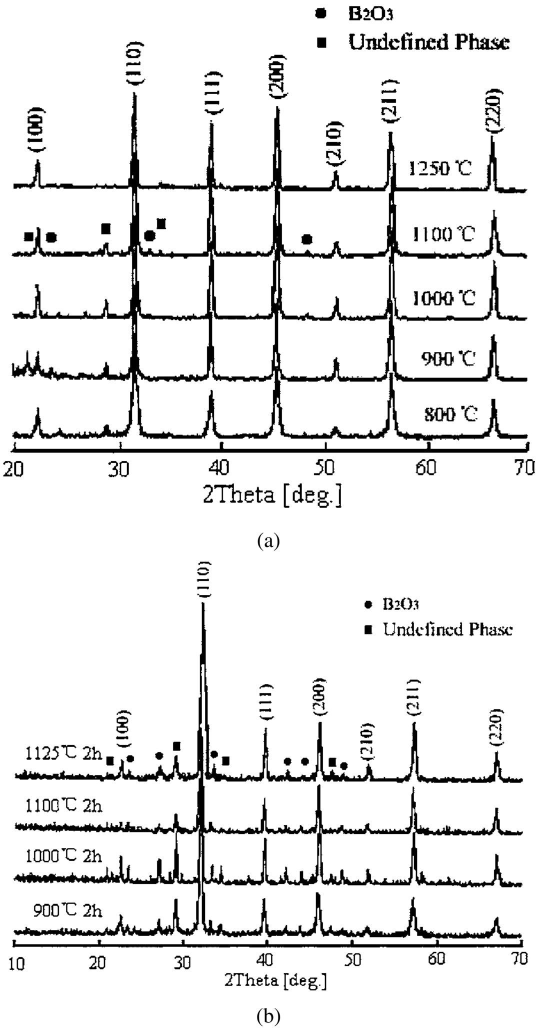


Figure 1 Flow chart of the $Sr_{0.6}Ba_{0.4}TiO_3$ glass ceramic powder.

Chemical Reagent Co.), tetrabutly titanate $Ti(C_4H_9O)_4$ (purity ≥ 98%, Shanghai Chemical Reagent Co.), tetraethy orthosilicate (TEOS, purity ≥ 99%, Shanghai Chemical Reagent Co.), and tributyl borate $B(OC_4H_9)_3$ (CP, Shanghai Chemical Reagent Co.) and acetic acid glacial, the procedure for fabricating these precursor solution is shown in Fig. 1. The dry gel was calcined at 900°C for 4 h. The obtained powders were crushed to a fine powder and then passed through a 300 mesh screen. The powder was pressed into disc-shaped pellets at an isostatic pressure of 200 MPa. No binder was used. The firing of the green pellets were performed in a Al_2O_3-covered crucible over a temperature range of 1100–1250°C for 2 h. After sintering, X-ray diffraction (Rigaku Co. Model D/max 2000) was employed to examine the phase constitution of the specimens. Microstructures of cross sections of the sintered samples were examined using a Shimadzu EPMA-8750.

To determine the dielectric properties of the samples, sintering samples were polished to a thickness of 0.3 mm, Ag-Pd paste was painted on the polished samples as the electrodes and fired at 750°C. The dielectric constant and dielectric loss of samples were measured with an HP4284A at the 10 kHz frequency.

The composition, sintered temperature, relative density and porosity are shown in Table I. The sintering temperatures were decreased with increasing of B_2O_3-SiO_2 glass content. The rigidity and intensity of BST samples with 1 mol%B_2O_3-SiO_2 sintered at 1250°C, 5 mol%B_2O_3-SiO_2 sintered at 1150°C, 10 mol% B_2O_3-SiO_2 sintered at 1125°C and 20 mol% B_2O_3-SiO_2 sintered at 1125°C as good as that of undoped BST sintered at 1340°C. The sintering temperatures were obviously decreased with increasing of B_2O_3-SiO_2 glass content. The sinter temperature of BST was not decreased when the SiO_2 was doped in BST sample. As we know that the B_2O_3-SiO_2 glass has a low melting point and makes liquid phases below the sintering temperature. Densities of sintered samples were measured by Archimedes's method. The



(a)

(b)

Figure 2 XRD patterns for (a) BSTS1 and (b) BSTS4 samples sintered at different temperature.

theoretical density ρ_{th} of the samples was determined using the atomic weight and lattice constants. The relative density was increased with increasing of B_2O_3-SiO_2 glass content. Further increasing the glass content, the relative density was decreased. The change trend was consistent with the change of relative density.

3. Results and discussion

Fig. 2 show the XRD patterns for samples BSTS1 and BSTS4 sintered at different temperature, respectively. The 1.0 mol% B_2O_3-SiO_2 glass doped sample sintering at 1250°C in Fig. 2 reveals no B_2O_3 or undefined phase peaks (as shown in Fig. 2a), indicating that B_2O_3 was volatilized partly and because B_2O_3 is a very light element, the small amount of B_2O_3 is not detected by XRD. However, when the glass content was higher and secondary phase peaks occur (as shown in Fig. 2b). Indicating that over-doped glass was not volatilized, remaining in the sample to form secondary phases.

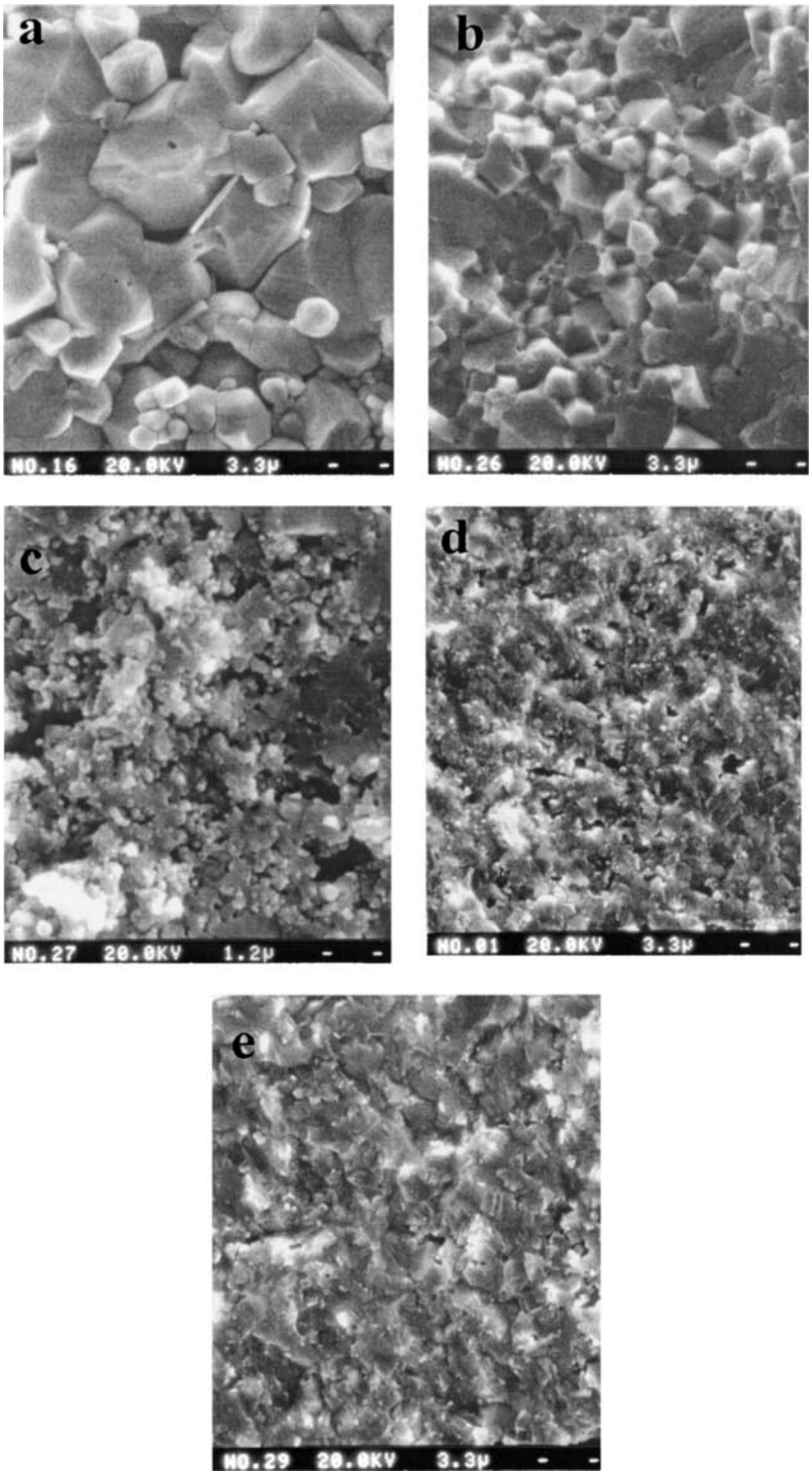


Figure 3 The microstructures of $Sr_{0.6}Ba_{0.4}TiO_3$ doped B_2O_3-SiO_2 glass samples: (a) 1340°C 2 h, (b) BSTS-1 1250°C 2 h, (c) BSTS-2 1150°C 2 h, (d) BSTS-3 1125°C 2 h and (e) BSTS-4 1125°C 2 h.

The sinter temperature of BST was not decreased when the SiO_2 was the only dopant in BST sample. It is known that the B_2O_3-SiO_2 glass has a low melting point and makes liquid phases below the sintering temperature. The liquid phases promote densification and coarsening at low temperature. It is obviously that the $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic doped B_2O_3-SiO_2 glass has a densification structure and smaller grain size (as shown in Fig. 3). Fig. 3 is the fracture surface of samples BSTS0, BSTS1, BSTS2, BSTS3 and BSTS4 sintered at different sintering temperatures. The glass phase can be seen clearly from the SEM images of higher glass content samples. The SEM images show a high density of pores in the higher glass content samples. Those results were consistent with the measurement dates of relative density and porosity.

In general, low-temperature sintering degrades dielectric properties, because the dielectric constant of the sintering aids is lower than that of the ceramics. Furthermore, reaction between the sintering aids and the ceramics causes the formation of a secondary phase with a low dielectric constant (BSTS4). However, some sintering aids improve dielectric properties because they incorporate into the grain and restrain the formation of a secondary phase (BSTS1).

The behavior of the dielectric constant of the samples with respect to temperature is shown in Fig. 4. (Ba, Sr)TiO_3 has a sintering temperature temperature of ~1350°C. As the glass content increases, the sintering temperature of $Ba_{0.6}Sr_{0.4}TiO_3$ doped B_2O_3-SiO_2 glass was decreased. As the sintering temperature increases, the dielectric constant increases largely, and the sample of BSTS-3 sintered at 1125°C shows a peak in the dielectric constant versus temperature, but the sample of BSTS-4 with more glass phase sintered at 1125°C does not show a clearly peak. Therefore, adding B_2O_3-SiO_2 glass to BST enhances sintering at low temperature and has no effect on the ferroelectric characteristics when the glass content is smaller than 20 mol%.

Fig. 5 shows the temperature dependence of the dielectric constant and dielectric loss as a function of the applied DC field for BSTS samples. The dielectric constant ε above the Curie temperature T_c can be represented as [11]

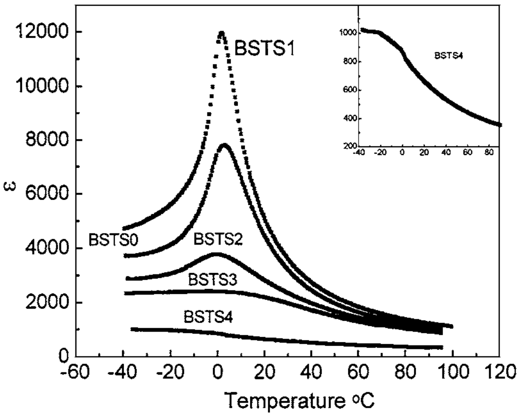


Figure 4 Temperature dependence of the dielectric constant in B_2O_3-SiO_2 glass doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics (a) BSTS-1 1250°C 2 h, (b) BSTS-2 1150°C 2 h, (c) BSTS-3 1125°C 2 h, and (d) BSTS-4 1125°C 2 h.

$$\frac{\varepsilon}{\varepsilon_0} = \frac{1}{\left(1 + a\varepsilon_0^3 E^2\right)^{1/3}}$$

where ε and ε_0 are the dielectric constant under zero DC field and under a bias E DC field, respectively, and a is the phenomenological coefficient. The dielectric constant ε decreases with increasing of the DC field. Dielectric loss was also slightly suppressed with increasing field. As shown in the Fig. 6, the influence of the loss factor of the samples on the DC field is minor.

It is suggested that there are two mechanisms for the DC field dependence of dielectric loss: $\tan\delta = \tan\delta_C + \tan\delta_R$ and $\tan_C$ can be expressed as [11]

$$\frac{\tan\delta_C}{\tan\delta_{C_0}} = \frac{1}{\left[1 + a(\tan\delta_{C_0})^3 E^2\right]^{1/3}}$$

where $\tan\delta_C$ is the intrinsic dielectric loss which is reduced by applying the DC field.

The other term $\tan\delta_R$ is the conduction loss that can be written as

$$\tan\delta_R = 1/(\omega R C_0)$$

where $\varepsilon(T, E)$ is the dielectric constant, which is a function of temperature and DC field. ω is the measuring frequency, C_0 is the geometrical capacitance. R is the resistance of the sample. As the DC field increases, the resistance decreases and the conduction loss increases. As the temperature increases, the DC field effect on $\tan\delta_C$ is suppressed, because of the decrease in the value of $a\varepsilon(T, 0)^3$ [12, 13]. The conduction loss increases because of the fact that ε and R both decreases. Therefore, $\tan\delta$ increases as the DC field increases at temperatures greater than T_b [14] and is not influenced by the DC field at T_b. The dielectric tunability, which is defined as the percentage of change of the dielectric constant under a specific DC field at the working temperature is often the concern in practical application.

The dielectric tunability D_t at DC field E and temperature T is defined as:

$$D_t(T, E) = \frac{\varepsilon(T, 0) - \varepsilon(T, E)}{\varepsilon(T, 0)} \times 100\%$$

Temperature dependence of the dielectric tunabilities at different DC field for samples with difference glass content shown in Fig. 2. At temperatures above 50°C, the dielectric tunability is reduced to below 10%. The Curie temperature was not observed when the glass content was 20% mol. The Curie temperature was broadened with increasing of glass content. The dielectric tunability decreases with increasing of glass content. It can be interpreted by considering the coexistence of the ferroelectric and paraelectric phases in the temperature range of diffuse phase transition [15, 16]. The nature of diffuse phase transitions for fine-grained ceramics cannot be described by the classical theory of ferroelectric phase transition, and their origin is not yet clear. However, it is quite natural that small ferroelectric particles show different dielectric properties from those of bulk crystals because the long-range Coulomb force plays an important role in them. The diffuse transition may be explained in terms of a stress-induced coexistence

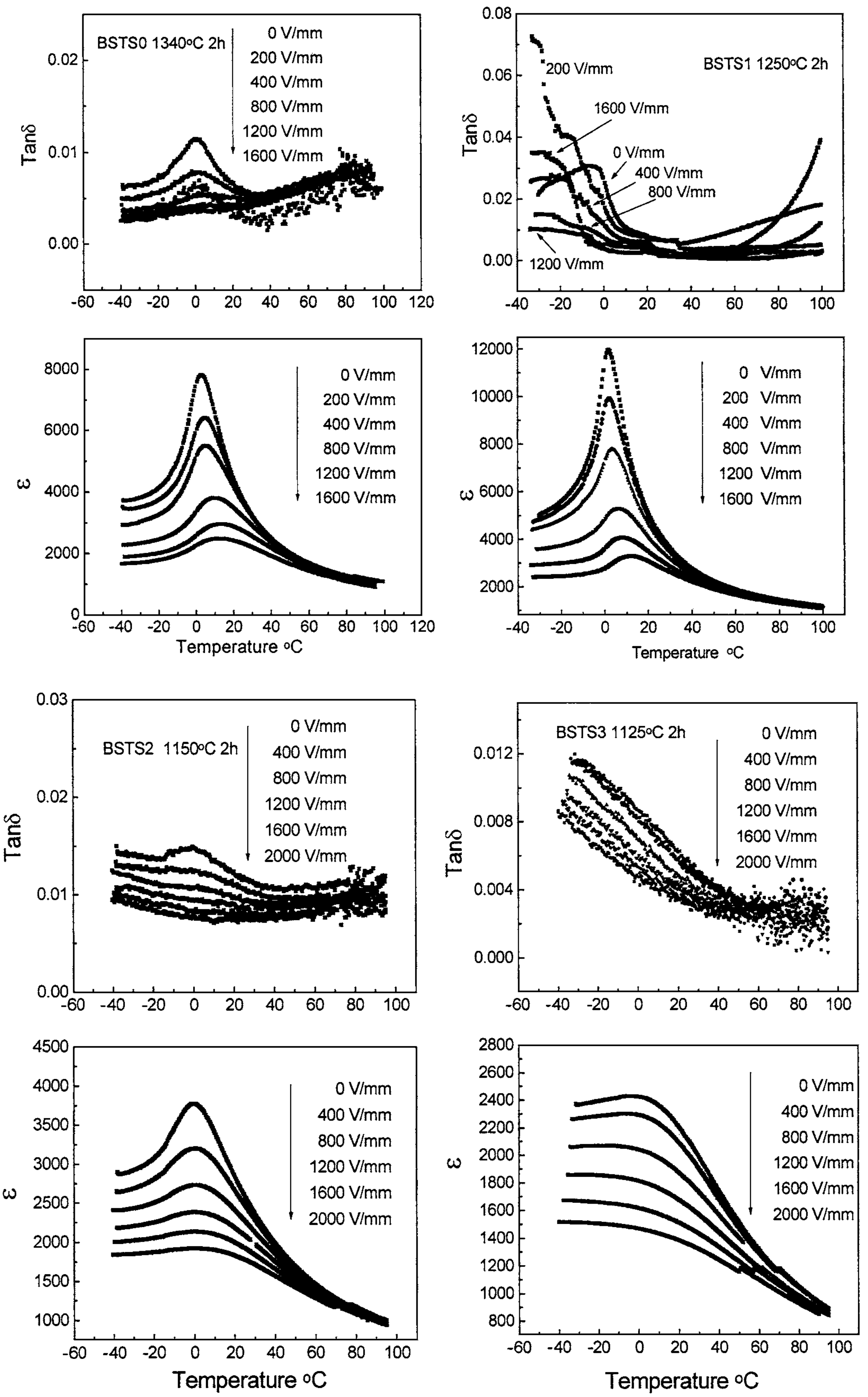


Figure 5 Temperature dependence of the dielectric constant and dielectric loss as a function of the applied DC field for the ceramics (a) BSTS-1 1250°C 2 h, (b) BSTS-2 1150°C 2 h and (c) BSTS-3 1125°C 2 h.

of cubic, tetragonal, orthorhombic and rhombohedral phases. The internal stress decreases as the grain size increases [17, 18]. Phase transitions seem to show such a broad dielectric constant maximum in samples sintered at lower temperatures, in which fine grains exist.

Fig. 5 is the relations of dielectric constant versus applying the DC field. The dielectric constant is reduced by applying the DC field especially in the neighborhood of the Curie peak. At temperature higher ($T_c + 10°C$, $T_c + 20°C$) or lower ($T_c - 10°C$, $T_c - 20°C$), the DC

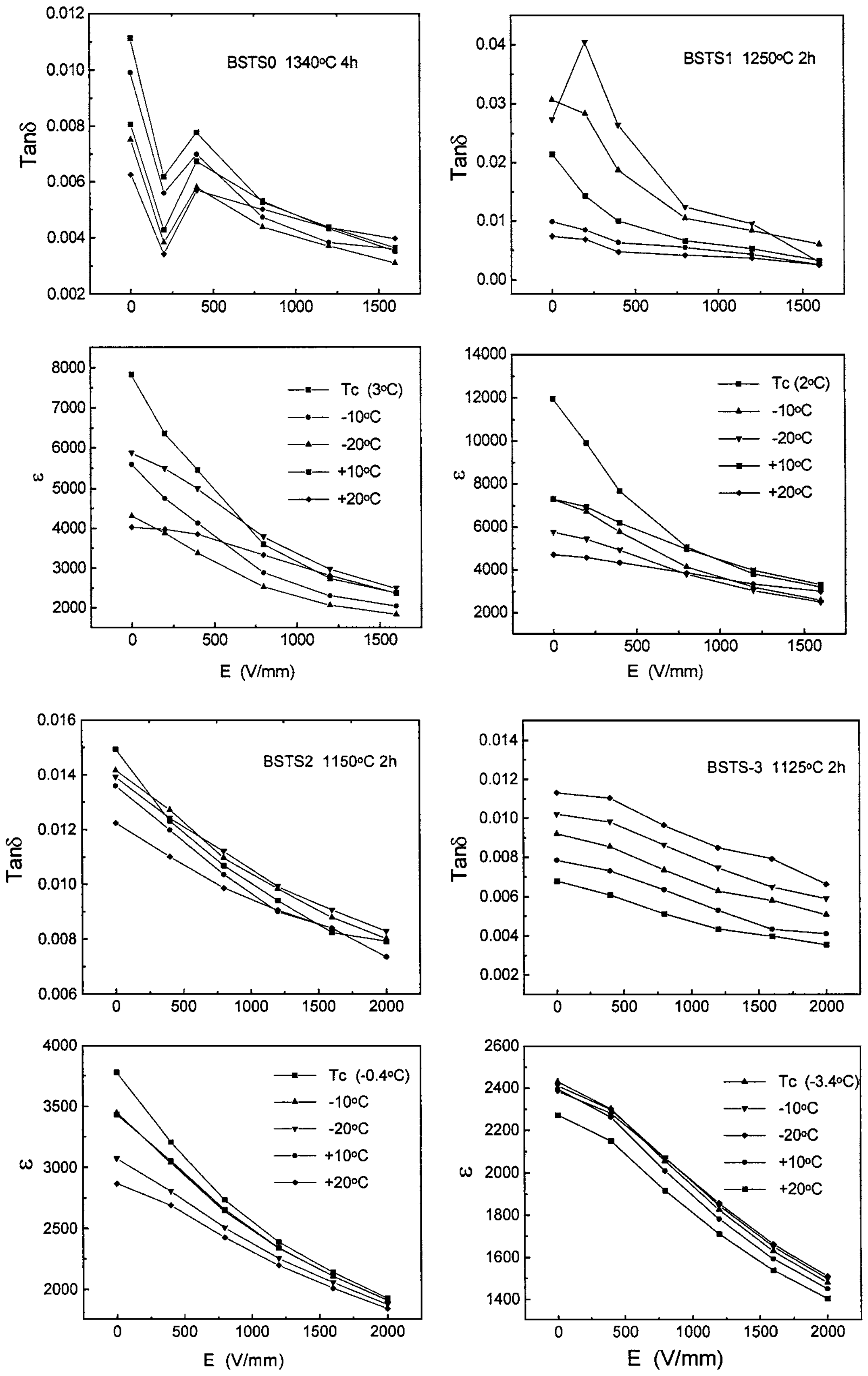


Figure 6 Dielectric constant and dielectric loss versus applied DC field for BSTS-1 sintered at 1250°C for 2 h, BSTS-2 sintered at 1150°C for 2 h and BSTS-3 1125°C for 2 h.

field is also effective for suppressing the dielectric constant. There are two linear regions for the change of dielctric constant with applying the DC field (shown in Fig. 6). One is the larger change rate in the range of 0 to 600 V/mm, the other is the smaller change rate in the range of 600 to 2000 V/mm for the sample of BSTS0 and BSTS1. The decrease of dielectric constant is linearly decreased with increasing of applying the DC field in the range of 0–2000 V/mm for the sample of BSTS2 and BSTS3. It is inferred that the dielectric tunability of BST may be affected by the grain size. In general, the higher sintering temperature, the larger grain size. The samples with larger grains have greater tunability [7]. The results indicate that the high tunability can

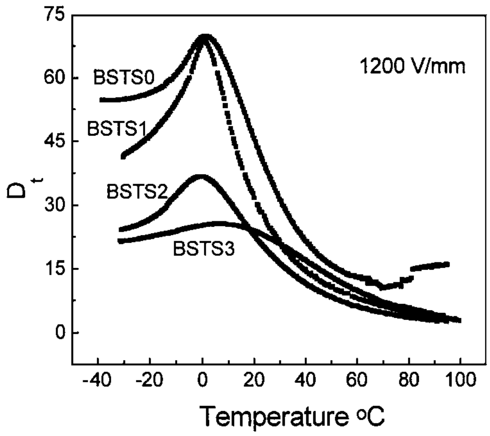


Figure 7 Temperature dependence of the dielectric tunability D_t at a 1200 V/mm DC field.

be obtained in the ferroelectric phase of BST ceramics and in non-ferroelectric phase, the tunability is smaller than that of in ferroelectric phase. The high tunability in ferroelectric phase originates from the polar clusters under DC field; and in non-ferroelectric phase the low tunability is attributed to the absence of the polar clusters [19, 20].

Fig. 7 is the temperature dependence of the dielectric tunability D_t at a DC field of 1200 V/mm with difference doped glass content. As shown in Fig. 7, that the dielectric constant is reduced by applying the DC field especially in the neighborhood of the Curie peak. At temperatures much higher than the transition peak, the DC field is ineffective for surpressing the dielectric constant.

4. Conclusion

$Ba_{0.6}Sr_{0.4}TiO_3$ doped different glass content was prepared by a sol-gel process. Adding B_2O_3-SiO_2 glass to BST promoted sintering at low temperature by the formation of liquid phase with a low melting point. The influence of the DC field on the loss factor is much less than that on the dielectric constant. With increasing of the applied voltage, the T_c was increased and the peaks were surpressed and broadened. As the glass content increases, The maximum dielectric constant and the percentage change of dielectric constant under a DC field decrease. The tunability of the sample is affected by the grain size and glass content in the $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic.

Acknowledgments

This project was supported by Chinese Science Fundamental Committee, Contract No. 59995320 and by the University key studies project of Shanghai.

References

1. C. M. CARLSON, T. V. RIVKIN, P. A. PARILLA *et al.*, *Appl. Phys. Lett.* **76**(14) (2000) 1920.
2. F. W. VAN KEULS, R. R. ROMANOFSKY, N. D. VARALJAY *et al.*, *Microwave Opt. Technol. Lett.* **20** (1999) 53.
3. V. N. KEIS, A. B. KOZYREV, M. L. KHAZOV, J. SOK and J. S. LEE, *Electron Lett.* **34** (1998) 1107.
4. F. A. MIRANDA, R. R. ROMANOFSKY, F. W. VAN KEULS, C. H. MUELLER *et al.*, *Ferroelectrics* **17** (1998) 231.
5. LONG WU, YIH-CHIEN CHEN, LI-JEN CHEN, YI-PING CHOU and YUAN-TU TSAI, *Jpn. J. Appl. Phys.* **38** (1999) 5612.
6. J. W. LIOU and B. S. CHIOU, *Materials Chemistry and Physics* **51** (1997) 59.
7. S. M. RHIM, S. K. HONG, H. J. BAK and O. K. KIM, *J. Amer. Ceram. Soc.* **83** (2000) 1145.
8. I. C. HO, *ibid.* **77** (1994) 829.
9. H. F. CHENG, T. F. LIN, C. T. HU and I. N. LIN, *ibid.* **76** (1993) 827.
10. I. C. HO, *ibid.* **77** (1994) 829.
11. K. M. JOHNSON, *J. Appl. Phys.* **33** (1962) 2826.
12. *Idem.*, *ibid.* **33** (1962) 2826.
13. R. VIANA, P. LUNKENHEIMER, J. HEMBERGER, R. BOHMER and A. LOIDL, *Phys. Rev. B: Condens. Mater.* **50** (1994) 601.
14. LONG WU, YIH-CHIEN CHEN, CHENG-LIANG HUANG, YI-PING CHOU and YUAN-TU TSAI, *J. Amer. Ceram. Soc.* **83** (2000) 1713.
15. S. CHATTOPADHYAY, P. AYYUB, V. R. PALKAR and M. MULTANI, *Phys. Rev.* B **52** (1995) 177.
16. S. CHATTOPADHYAY, P. AYYUB, V. R. PALKAR, A. V. GURJAR, R. M. WANKAR and M. MULTANI, *J. Phys.: Condens. Matter.* **9** (1997) 8135.
17. W. R. BUESSEM, L. E. CROSS and A. K. GOSWAMI, *J. Amer. Ceram. Soc.* **49**(1) (1966) 33.
18. *Idem.*, *ibid.* **49**(1) (1966) 36.
19. CHEN ANG, A. S. BHALLA and L. E. CROSS, *Phys. Rev.* B **64** (2001) 18104.
20. CHEN ANG, L. E. CROSS, RUYAN GUO and A. S. BHALLA, *Appl. Phys. Lett.* **77**(5) (2000) 732.

Received 11 April 2001
and accepted 25 April 2002