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Dielectric and tunable properties of barium strontium titanate ceramics under the stresses

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ABSTRACT

The external stress dependence of dielectric and tunable properties of $Ba_xSr_{1-x}TiO_3$ ($x = 0.65$) ceramics has been investigated. The results reveal that the Curie peaks of samples are suppressed and broadened, the Curie temperature (T_c) is slightly shifted to lower temperature with an increase of external stress. Correspondingly, the tunability decreases from 66.6% to 58.8% in the vicinity of cubic–tetragonal (C–T) phase transition at an applied DC electric field of 10 kV/cm. These results could be useful for the design of devices and practical applications of $Ba_xSr_{1-x}TiO_3$ ceramics.

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1. Introduction

$Ba_xSr_{1-x}TiO_3$ (BST), as one of the most important ferroelectric materials, attracts extensive interests of researchers because of its high tunability and low dielectric loss. Therefore, it is widely considered as an excellent candidate for potential use in the field of telecommunications, wireless communication devices and tunable devices (such as multilayer ceramic capacitors, phase shifters, delay lines, and so on) [1–3]. The Curie temperature (T_c) of BST could be tailored by altering mole ratio of Ba/Sr, or ions doping concentrations, etc. [4–7] in order to meet various requirements of practical applications. Actually, in the field of some applications, materials itself or devices could be exposed to the self-induced internal stress or external stress. For example, at the high sintering processing, multilayer ceramic capacitors usually undergo a substantial stress among layered structure materials, because of mismatch of thermal expansion coefficient, lattice constant or growth stresses [8,9]. It has been confirmed that ferroelectric properties of ceramics depend strongly on external stress, especially for stress-sensitive Pb-based perovskite materials (PZT, PMN-PT, etc.) [10,11]. $BaTiO_3$-based ceramics or single-crystal subjected to external pressure have also been widely reported by Samara [12], Shirane and Sato [13], Fritz [14], and Duan et al. [15]. The results show that a linear shift of T_c toward lower temperature under the hydrostatic pressure was observed, while under the uniaxial-stress, T_c was shifted to higher temperature, simultaneously, the peaks of ferroelectric-paraelectric phase transition broadened, and the dielectric constant decreased due to domain reorientation suppression for both.

To our best of knowledge, the dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics under external stress have not been reported yet in the literatures. Therefore, it is necessary to determine the influences of external stresses on dielectric properties of BST materials, and helpful to further understand the dielectric response mechanism under stress conditions. The experiments were performed on ceramic samples of pure $Ba_{0.65}Sr_{0.35}TiO_3$ due to its Curie temperature closer to room temperature and strong temperature sensitivity. The influences of external stress on dielectric properties of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramic are investigated.

2. Experimental

$Ba_{0.65}Sr_{0.35}TiO_3$ ceramics were fabricated by the conventional solid-state reactions according to the stoichiometric ratio. The $BaTiO_3$ (99.9%) and $SrTiO_3$ (99.9%) powders with average particle sizes of 100 nm were mixed with alcohol and zirconia grinding media in the polypropylene bottles, then milled for 24 h, dried at 100 °C, followed by calcinating at 1100 °C for 4 h in air. Subsequently, the dried mixtures were granulated with 8 wt% polyvinyl alcohol binder, then pressed into disk-shaped pellets and rectangular blocks for dielectric property measurements under stress-free and external stress, respectively. At last, the green pellets were sintered at 1350 °C for 4 h in air.

The sintered samples were polished to 10 mm in diameter, 0.5 mm in thickness for circular pellets, the dimensions of L (length)/10 mm, H (height)/0.5 mm, W (width)/2 mm for rectangular blocks. Gold electrodes were sputtered on both sides ($L \times W$ surface) of samples. microstructure analyses of samples were characterized by a scanning electron microscopy (SEM) (JSM EMP-800, JEOL, Tokyo, Japan). Average grain size of samples was determined from SEM micrographs of polished specimens by a linear intercept method. Dielectric constant as a function of temperature was measured using an E4980A precision LCR meter (Agilent, Palo Alto, CA). The dielectric constant vs. direct current (DC) bias voltage was tested using a Keithley 2410 (Cleveland, OH) high voltage source and TH2816A LCR (Changzhou, China) analyzer.

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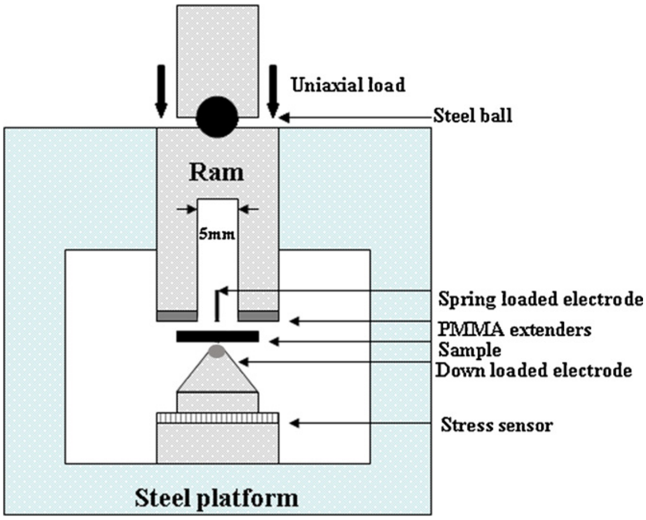

Fig. 1. A schematic illustration of the experimental set-up under applied stress.

In order to study the effects of external stresses on dielectric properties of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics, a compressometer was constructed. The schematic illustration of experimental set-up with stress and electric field was shown in Fig. 1. The compressometer cell included a cylindrical stainless-steel ram, a loading platform and a stainless-steel cone indenter (cone angle 120°, tip radius 0.2 mm). Samples placed between ram and indenter were subjected to the stress, which was generated by tightening the screw to drive the ram. The steel ball was placed between the screw and the ram in order to relieve rotation of the ram. PMMA (polymethyl methacrylate) plates were used to avoid shear deformations resulting from elastic mismatch between metal ram and samples. Thin Mylar films were adhered to the PMMA plate surface of the metal ram to fill any irregular surface. Fig. 1 showed that samples were suffered from force in three-point bending, and values of the applied stress parallel to electric field direction were measured by a suitable range stress sensor with a gage. The spring probes installed in the ram and the cone indenter as upper and lower electrodes were used to transmit electric signals. Furthermore, in this equipment, the variations of dielectric constant resulting from geometrical deformation under stress could be negligible ($\Delta\varepsilon < 0.9\%$) according to the expression, $\Delta\varepsilon = \varepsilon P(1+2\upsilon)/E$, where P is applied stress, υ is Poisson ratio, E is Young modulus [16].

3. Results and discussion

The SEM micrograph of pure $Ba_{0.65}Sr_{0.35}TiO_3$ ceramic sample is presented in Fig. 2. The sample shows an uniform and homogeneous morphology, consists of average grain size around 12.3 μm. No abnormal grain growth is observed. According to Park et al., the dielectric response for small grained -size $BaTiO_3$-based ceramics (<2 μm) were less sensitive to external pressure in comparison with that of large grained size (>2 μm) [17]. So samples with larger grains is helpful to investigate dielectric properties under the action of an applied stress, regardless of the influences of grain size-induced internal stress.

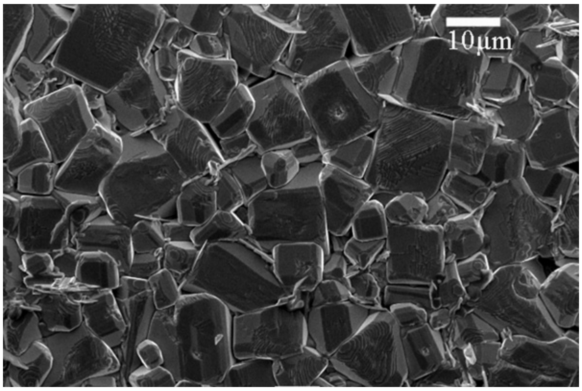

Fig. 2. SEM image of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics sintered at 1350 °C for 4 h.

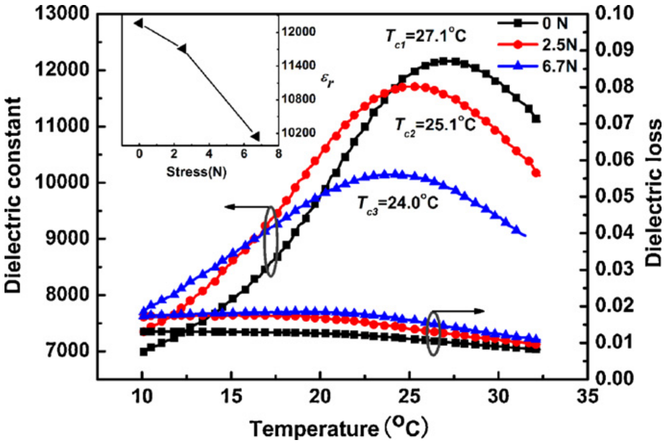

Fig. 3. Temperature dependence of dielectric constant and loss for $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics at different stresses parallel to the electric field at 10 kHz. The inset is the dielectric constant (ε_r) in Curie peaks of temperature dependence of dielectric constant and loss at different stresses.

Fig. 3 gives the temperature dependence of the dielectric constant and loss of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics at 10 kHz under different stress levels. The temperature range measured is changed from 10 to 33 °C to minimize effects of the thermal expansion on dielectric response between samples and stress sensor. As depicted in the inset of Fig. 3, there is an obvious change in dielectric constant and loss under external stress. The maximum of dielectric constant decreases from 12165 to 10145 with increasing external stress. However, dielectric loss increases continuously with increasing stress. Similar experimental phenomena have been obtained in Fe^{3+}/Nb^{5+} doped $BaTiO_3$ ceramics [18], and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ceramics [19], where dielectric constant decreases, and dielectric loss increases with increasing the external stresses. Interestingly, the stress-induced shift of cubic–tetragonal (C–T) phase transition of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics was observed. The Curie temperature (T_c) shifts to a lower temperature from 27.1 °C to 24.0 °C, as increasing the external stress from 0 to 6.7 N. The changes of T_c under external stress is the similar case of $BaTiO_3$ [12] and $(Ba,Ca)TiO_3$ [14] ceramics under external stress, it is suggested that the stress-induced shift of T_c could be related to the lattice variations, i.e., the external stresses result in variations of unit-cell volume [20,21]. In this study, all samples are subjected to a pressure resulting from three-point bending (Fig. 1), which may lead to a deformation of lattice, then bring the decrease of ferroelectric–paraelectric phase transition temperature. Furthermore, it is found that the Curie peaks are obviously broadened when the stress is increased up to 6.7 N. Such the diffusion characterization of Curie peaks is analogous to that observed in fine-grain $BaTiO_3$ ceramics under free of stress, it indicates that stress may be one of origins of the diffuse phase transition (DPT) [22]. The diffuseness degree of phase transition can also be described by an empirical parameter ΔT:

$$\Delta T = T_{0.9\varepsilon_m(10\,kHz)} - T_{\varepsilon_m(10\,kHz)}, \tag{1}$$

where ε_m is the maximum value of the dielectric constant, and $T_{0.9\varepsilon m}$ and $T_{\varepsilon m}$ are the temperature corresponding to 90% of dielectric constant maximum (ε_m) [23]. The ΔT parameters obtained from Eq. (1) are listed in Table 1. It can be seen that the degree of diffuseness increases gradually with increasing the external stress, and the curie peaks are more depressed.

In conclusion, Curie peaks are depressed, broadened and shifted to lower temperature as a result of increasing stress. The behavior can be interpreted by non-180° domain-reorientation processes.

Table 1
Dielectric properties of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics at different stresses.

Stress(N)	Curie temperature (°C) (T_c)	ε_r at T_c(10 kHz)	Diffused level (°C) (ΔT)
0	27.1	12165	4.7
2.5	25.1	11710	6.1
6.7	24.0	10145	7.2

The applied stress blocks ferroelectric domains of BST ceramics in the vicinity of T_c aligned with their polar axes (c axes) to rearrange (non-180° domains). Consequently, the contributions of domains to dielectric response parallel to stress direction are reduced. This is also consistent with Devonshire phenomenological theory and free-energy equation [24]. And, under external stress, the growth of micropolar regions near Curie peaks may be responsible for diffusion of Curie peaks. Besides, the external pressure also generates some defects, such as the density of dislocation and point defects, it could be the origin of increasing dielectric loss under applied stress [25].

The effect of external stress on DC bias field dependence of dielectric constant is shown in Fig. 4. It is measured at 10 kHz and 26 °C (T_c = 27.1 °C) with different stress levels. As it can be seen, the changes of dielectric constant and loss with external stresses at zero electric field are consistent with the depicted in Fig. 3, because of stress-induced domain wall suppression. The dielectric constant of samples returns to its original value when the stress is removed. For a given stress, the dielectric constant vs. electric field displays an nonlinear behavior, and with increasing electric field levels up to 10 kV/cm, all the ε–E curves almost overlap together. With further increasing electric field (>10 kV/cm), the external stress has not significantly influence on changes of dielectric constant (not shown here). For the detailed description of the trend in dielectric constant vs. electric field under an action of applied stress, the equation is adopted as follows:

$$T\ (\text{tunability}) = \frac{[\varepsilon(0) - \varepsilon(E)]}{\varepsilon(0)} \qquad (2)$$

where $\varepsilon(0)$ and $\varepsilon(E)$ are the dielectric constants at zero and applied electric field, respectively. The values of tunability are directly related to the amount of domains participating in the polarization switching process under applied electric field. The calculated values of T are shown in Fig. 5. The tunability monotonously reduces, it is in the range from 66.6% to 58.8% with gradually increasing stresses to maximum 7.3 N. Such trends are consistent with that Song et al. reported [8]. The decrease of tunability also indicates that the amount of domain switching decreases due to the stress-induced domain wall suppression. In other words, the electric field as well as the external stress has obviously influences on the dielectric response of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics near T_c [26]. At lower electric field, the stress is prodominant in determining the dielectric response through suppressing the domain switching. With increasing the electric field, amount of the domain switching is gradually saturated, as illustrated in Fig. 4. Similar phenomenon is also observed in the ε–E curves under different temperatures and stress-free, as shown in Fig. 6. Finally, the results above could be useful in the design of devices and practical applications of the $Ba_xSr_{1-x}TiO_3$ ceramics. It is of particular concern in the vicinity of the ferroelectric–paraelectric transitions.

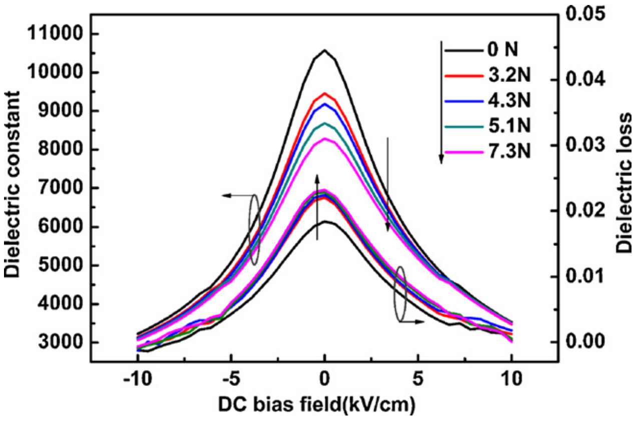

Fig. 4. DC electric field dependent dielectric constant and loss for $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics along. stress direction at different stresses at 10 kHz and 26 °C (arrows represent the direction of increasing the stress).

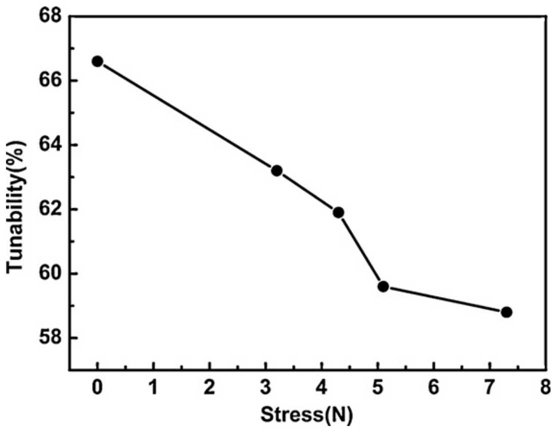

Fig. 5. The calculated tunability using Eq. (2) as a function of applied stresses for $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics.

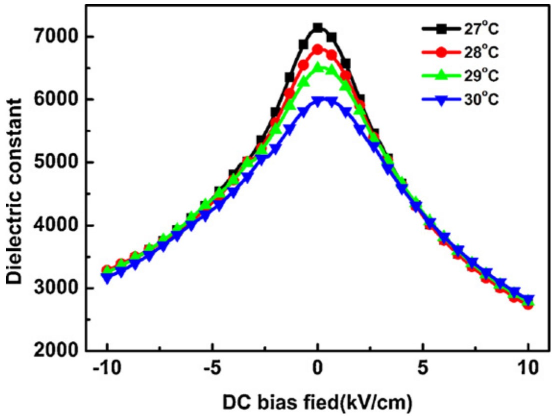

Fig. 6. DC electric field dependent dielectric constant at different temperatures at 10 kHz under stress-free.

4. Conclusions

In the present study, the dielectric properties of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics with different stress applied parallel to DC electric field were investigated. It is concluded that the external stress had an obviously influences on dielectric response of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics. The shift of T_c to lower temperature was observed due to stress-induced phase transition. With increasing external stresses, the Curie peaks were suppressed and broadened, the dielectric loss increased. Tunabilities in the vicinity of Curie temperature were remarkably decreased from 66.6% to 58.8% due to stress-induced domain wall motion suppression.

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References

[1] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, J. Electroceram. 11 (2003) 5.

[2] H. Abdelkefi, H. Khemakhem, G. Vélu, J.C. Carru, R. Von der Mühll, J. Alloys Compd. 399 (2005) 1.

[3] R. Reshmi, A.S. Asha, P.S. Krishnaprasad, M.K. Jayaraj, M.T. Sebastian, J. Alloys Compd. 509 (2011) 6561.

[4] T. Wang, F. Gao, G.X. Hu, C.S. Tian, J. Alloys Compd. 504 (2010) 362.

[5] J.J. Zhang, J.W. Zhai, X.J. Chou, J. Shao, X. Lu, X. Yao, Acta Mater. 57 (2009) 4491.

[6] J.D. Cui, G.X. Dong, Z.M. Yang, J. Du, J. Alloys Compd. 490 (2010) 353.

[7] W. Li, Z.J. Xu, R.Q. Chu, P. Fu, J.G. Hao, J. Alloys Compd. 499 (2010) 255.

[8] S.N. Song, J.W. Zhai, L.N. Gao, X. Yao, Appl. Phys. Lett. 94 (2009) 052902.

[9] T.M. Shaw, Z. Suo, M. Huang, E. Liniger, R.B. Laibowitz, J.D. Baniecki, Appl. Phys. Lett. 75 (1999) 2129.

[10] P.M. Chaplya, G.P. Carman, Appl. Phys. Lett. 90 (2001) 5278.

[11] J. Zhao, A.E. Glazounov, Q.M. Zhang, Appl. Phys. Lett. 74 (1999) 436.

[12] G.A. Samara, Phys. Rev. 151 (1966) 378.

[13] G. Shirane, K. Sato, J. Phys. Soc. Jpn. 6 (1951) 20.

[14] I.J. Fritz, J. Appl. Phys. 49 (2) (1978) 788.

[15] Y.F. Duan, G. Tang, L.X. Qin, L.W. Shi, J. Alloys Compd. 507 (2010) 513.

[16] R. Yimnirun, M. Unruan, Y. Laosiritaworn, S. Ananta, J. Phys. D 39 (2006) 759.

[17] Y. Park, K. Cho, H.G. Kim, J. Am. Ceram. Soc. 81 (1998) 1893.

[18] M. Unruan, T. Sareein, J. Tangsritrakul, S. Prasertpalichatr, A. Ngamjarurojana, S. Ananta, R. Yimnirun, J. Appl. Phys. 104 (2008) 124102.

[19] M. Unruan, A. Ngamjarurojana, Y. Laosiritaworn, S. Ananta, R. Yimnirun, J. Appl. Phys. 104 (2008) 034101.

[20] L. Zhang, W.L. Zhong, C.L. Wang, P.L. Zhang, Y.G. Wang, J. Phys. D: Appl. Phys. 32 (1999) 546.

[21] Y. Kobayashi, S. Endo, L.C. Ming, K. Deguchi, T. Ashida, H. Fujishita, J. Phys. Chem. Solids 60 (1999) 57.

[22] Z. Zhao, V. Buscaglia, M. Viviani, M.T. Buscaglia, L. Mitosertiu, A. Testino, M. Nygren, M. Johnsson, P. Nanni, Phys. Rev. B 70 (2004) 024107.

[23] C. Ang, Z. Yu, P.M. Vilarinho, J.L. Baptista, Phys. Rev. B 57 (1998) 7403.

[24] A.F. Devonshire, Adv. Phys. 3 (1954) 85.

[25] J. Suchanicz, K. Wojcik, Mater. Sci. Eng. B 104 (2003) 31.

[26] J.W. Zhai, H. Chen, C.C. Chou, S.I. Raevskaya, S.A. Prosandeev, I.P. Raevski, J. Alloys Compd. 509 (2011) 6113.