

Dielectric properties of $(\text{Ba}_{1-2x}\text{Sr}_x\text{Ca}_x)\text{TiO}_3$ ferroelectric ceramics

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Abstract Ferroelectric ceramics of $(\text{Ba}_{1-2x}\text{Sr}_x\text{Ca}_x)\text{TiO}_3$ ($0 \leq x \leq 0.30$) were prepared by a routine solid-state reaction technique. Co-substitution of Sr^{2+} and Ca^{2+} for Ba^{2+} with equal mole in BaTiO_3 restrain the maximal dielectric constant K_m strongly when $0.2 \geq x > 0$. However, composition $(\text{Ba}_{0.4}\text{Sr}_{0.3}\text{Ca}_{0.3})\text{TiO}_3$ shows the higher maximal dielectric constant. With increasing Sr and Ca content x , temperature T_m of the maximal dielectric constant K_m shifts to low temperature and all selected compositions for study exhibit a broad phase transition temperature range. The composition $(\text{Ba}_{0.4}\text{Sr}_{0.3}\text{Ca}_{0.3})\text{TiO}_3$ presents characteristics of ferroelectric relaxor, value of K_m decreases and temperature T_m increases with increasing frequency.

Keywords $(\text{Ba}_{1-2x}\text{Sr}_x\text{Ca}_x)\text{TiO}_3$ · Dielectric properties · Relaxation behavior · Diffuse phase transition

1 Introduction

Barium strontium titanate (BST) has been widely studied due to its potential application in electronic ceramics field [1–4], especially in tunable microwave devices [5, 6]. However, the relatively high dielectric loss and large temperature dependence are problems for BST ceramics.

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MgO doping has been used in BST bulk ceramics and thin films to suppress dielectric constant and dielectric loss [6, 7]. Previous studies on the dielectric properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ solid solution ceramics have shown that the compositions with $x < 0.8$ exhibited normal ferroelectric behavior while a relaxor ferroelectric behavior was observed in the compositions with $x > 0.8$ [8, 9].

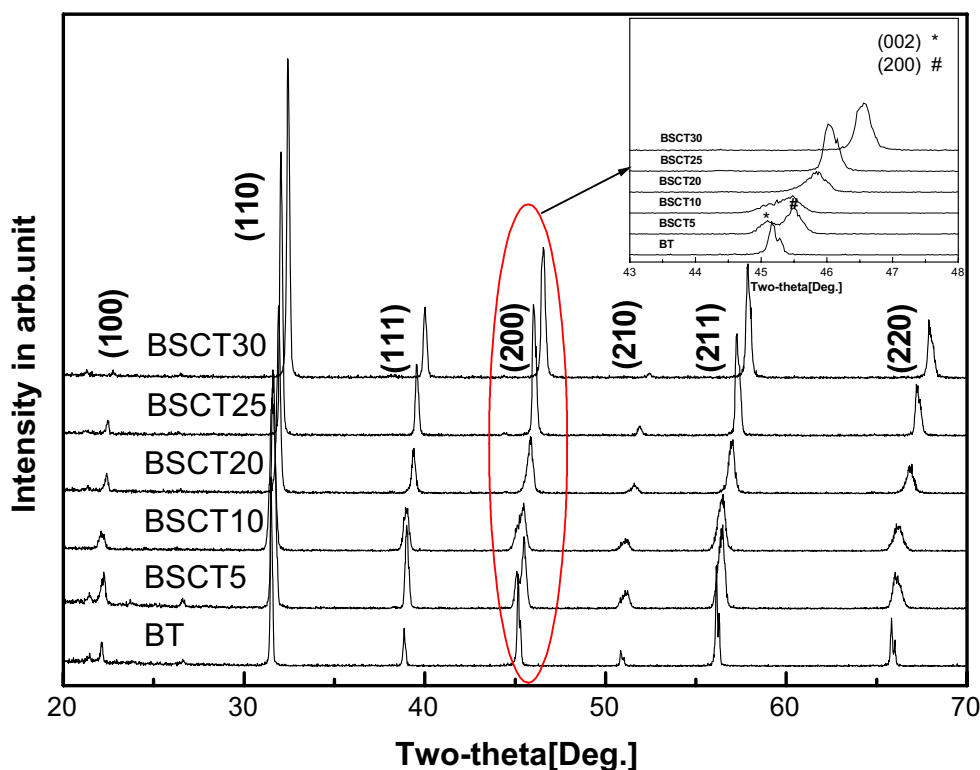
CaTiO_3 has been known as a typical depressor in BaTiO_3 ceramics, which represents the origin of significant suppression on dielectric loss and temperature coefficient of dielectric constant. On the contrary, it has a little effect on temperature T_m of the peak dielectric constants [10]. Chen et al [11] recently investigated dielectric properties and field dependence of dielectric constant in $(\text{Ba,Ca})\text{TiO}_3$ ferroelectric ceramics. In their study, $(\text{Ba,Ca})\text{TiO}_3$ ferroelectric ceramics with a very small dielectric loss was obtained, but the tunability is not high. The recent and past publications have shown that the diffuse phase transition (DPT) behavior was rarely observed in solid solutions with substitution of barium ions such as $(\text{Ba,Ca})\text{TiO}_3$ solid solutions [10, 12], where the dielectric constant curves were sharp and the dielectric constant maximum temperatures are frequency independent.

In this work, $(\text{Ba}_{1-2x}\text{Sr}_x\text{Ca}_x)\text{TiO}_3$ ceramics were prepared and the dielectric properties were investigated. A typical ferroelectric relaxation behavior is observed in composition $(\text{Ba}_{0.4}\text{Sr}_{0.3}\text{Ca}_{0.3})\text{TiO}_3$. The relationship between ferroelectrics with DPT and relaxor ferroelectrics is discussed.

2 Experimental procedure

$(\text{Ba}_{1-2x}\text{Sr}_x\text{Ca}_x)\text{TiO}_3$ (BSCT, $0 \leq x \leq 0.30$) ceramic samples were prepared by a routine solid-state reaction technique. (The compositions chosen for study are BaTiO_3 (BT),

Fig. 1 XRD patterns of BSCT ceramics



$\text{Ba}_{0.9}\text{Sr}_{0.05}\text{Ca}_{0.05}\text{TiO}_3$ (BSCT5), $\text{Ba}_{0.8}\text{Sr}_{0.1}\text{Ca}_{0.1}\text{TiO}_3$ (BSCT10), $\text{Ba}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{TiO}_3$ (BSCT20), $\text{Ba}_{0.5}\text{Sr}_{0.25}\text{Ca}_{0.25}\text{TiO}_3$ (BSCT25) and $\text{Ba}_{0.4}\text{Sr}_{0.3}\text{Ca}_{0.3}\text{TiO}_3$ (BSCT30). Stoichiometric amount of reagents BaCO_3 , SrTiO_3 , CaCO_3 and TiO_2 powders were wet mixed by ball milling in alcohol for 4 h using agate balls in a planetary mill. After drying, the mixtures were presintered at 1100°C for 4 h. The presintered powders were wet ball-milled for 4–5 h and dried again. Pellets of 10 mm in diameter and ~1 mm thick were pressed using 5% PVA. The binder was burnt out by slow heating up 500°C for 3–4 h. The samples were fired between 1280 and 1450°C in air for 3 h with heating rates of $200^\circ\text{C}/\text{h}$. The ceramic samples were cooled with the furnace.

Crystal structures of ceramic samples were analyzed by X-ray diffraction (XRD) at room temperature using $\text{CuK}\alpha$ radiation. Microstructural development examined by scanning electron microscopy (SEM). Before dielectric measurements, silver electrodes were painted on polished surfaces of the samples, and then fired at 810°C for 10 min as electrodes. Dielectric properties at frequencies ranging from 100 to 100 kHz were measured with an Agilent 4284A LCR meter, as samples were heated at a rate of $2^\circ\text{C}/\text{min}$ from -150 to 200°C .

3 Results and discussion

Figure 1 shows XRD patterns of BSCT ceramics. All samples present a single perovskite structure. BT and BSCT5 have

tetragonal symmetry, BSCT10 and BSCT20 show mixture of tetragonal and cubic phases, BSCT25 and BSCT30 are cubic symmetry. The magnified portion around peak (200) highlights further the phase transition with the reduced splitting with increasing x . A clear shift of the diffraction peaks to higher two-theta values with increasing x can also be seen in the inset of Fig. 1, an indication of a decrease of the unit cell volume with increasing x , consistent with that the radius of Ca^{2+} ions and Sr^{2+} ions are smaller than that of Ba^{2+} ions.

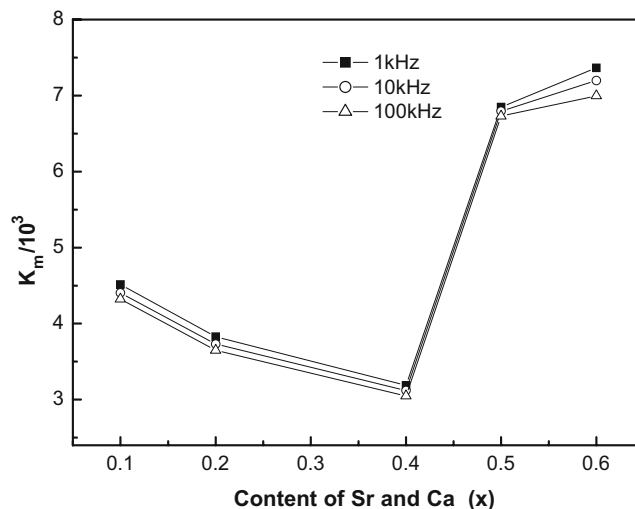


Fig. 2 Maximal dielectric constant of BSCT ceramics vs Sr and Ca contents

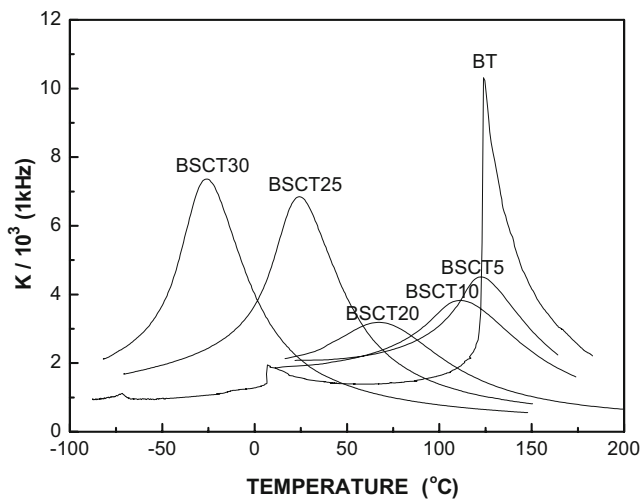


Fig. 3 Temperature dependence of dielectric constant of BSCT ceramics at 1 kHz

The plots of maximal dielectric constant K_m vs content of Sr and Ca for BSCT ceramics is shown in Fig. 2. Temperature dependence of dielectric constant for the BSCT ceramics at 1 kHz is shown in Fig. 3. With increasing Sr and Ca content, the maximal dielectric constant decreases till $x=0.2$, which may be due to the suppressing effect of CaTiO_3 on dielectric constant [10]. Moreover, frequency dependence of dielectric constant increases with increasing x . While compositions BSCT25 and BSCT30 show the higher maximal dielectric constant. With increasing x , the temperature T_m of the maximal dielectric constants of BSCT ceramics was shifted to low temperature, the phase transition region became diffused.

Fig. 4 Temperature dependence of dielectric constant and loss for BSCT25 and BSCT30 ceramics at various frequencies

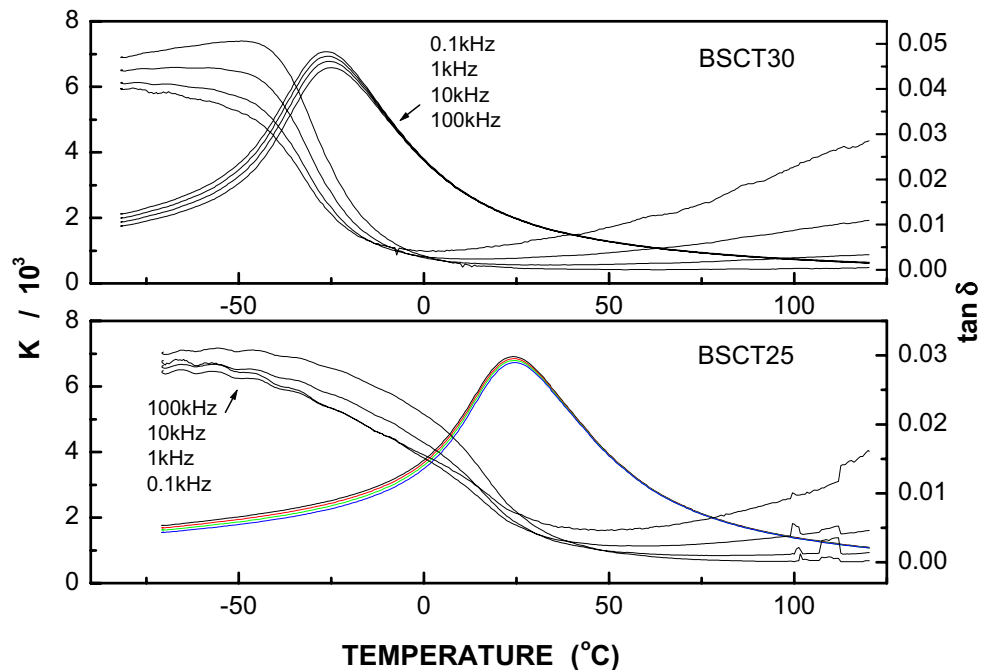


Figure 4 shows temperature dependence of the dielectric constant and dielectric loss at various frequencies for ceramics BSCT25 and BSCT30. The dielectric peak is found to be broadened over a certain temperature interval. The T_m of the ceramics BSCT25 is independent of frequency in the range of 0.1 k and 100 kHz. This suggests that the BSCT25 is ferroelectric with diffuse phase transition. While the dielectric constant of ceramics BSCT30 shows a phenomenon known as frequency dispersion, the K_m decreases and the T_m shifts towards higher temperatures with increasing frequency. These are the characteristics of relaxor ferroelectrics. Though the compositions of BSCT25 and BSCT30 are close to each other, their dielectric behavior is somewhat different. One is ferroelectric with DPT, the other is relaxor ferroelectric.

Uchino and Nomura [13] proposed a modified Curie-Weiss law to describe the diffuseness of the phase transition as,

$$1/K - 1/K_{\max} = (T - T_m)^\gamma / C \tag{1}$$

where K and K_m are the dielectric constant and its maximum, respectively, T is the temperature; T_m is the temperature of K_m , C and γ are assumed to be constant. It is believed that the parameter γ close to 1 suggests normal ferroelectrics, while close to 2 suggests relaxor ferroelectrics. We obtained the parameter $\gamma=1.48$ and $\gamma=1.82$ for BSCT25 and BSCT30, respectively, by fitting to the experimental data. These results suggest that BSCT30 is most probably a relaxor ferroelectric and BSCT25 is a mediocrity between normal ferroelectrics and a relaxor ferroelectric.

Dielectric relaxation behavior has been observed in $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ [14], $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$ [15] and $(\text{Ba}_{1-x}\text{Sr}_x)_{1-1.5y}\text{Bi}_y\text{TiO}_3$ [16], which is similar to that observed in ferroelectric relaxors. The relaxor behavior of them was interpreted to be due to the off-center location of Ca^{2+} or Bi^{3+} in the A sites. For Ca^{2+} doped SrTiO_3 [14], Ca^{2+} ions with the same charge as A sites ions should mainly occupy this site, some of the Ca^{2+} ions may also be located at B sites like Ti^{4+} ions sites, to balance the charge misfit, V_O vacancies may occur and form a $\text{Ca}^{2+}\text{-V}_\text{O}$ neutral center with Ca^{2+} ions. Such the dipoles were formed, thus set up local electric fields. According to this idea, the DPT behavior should be observed in $(\text{Ba,Ca})\text{TiO}_3$ solid solutions. Unfortunately, it is not found in the published literature. Though it has been observed in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ [8] solid solutions with rich SrTiO_3 content, which may be regarded as Ba substituting for Sr in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, the dielectric relaxation observation could not be attributed to this mechanism. Because Ba^{2+} has a bigger ionic radius compared to Sr^{2+} and should not be an off-center ion. Whether the dielectric relaxation observation of $(\text{Ba}_{1-2x}\text{Sr}_xCa_x)\text{TiO}_3$ solid solution could be attributed to this mechanism or not, which depend on the experimental and theoretical support. The related relaxation mechanism of investigation is being further studied.

4 Conclusions

The temperature T_m of BSCT ceramics shifted to lower temperature, and dielectric frequency dispersion increases

with increasing x . The BSCT ceramics show diffuse phase transition without typical dielectric relaxation behavior when $x < 0.25$. The composition $(\text{Ba}_{0.4}\text{Sr}_{0.3}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.30$) presents characteristics of ferroelectric relaxor.

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References

1. R. Wang, Y. Inaguma, M. Itoh, *Mater. Res. Bull.* **36**, 1693 (2001)
2. B. Su, W.T. Button, *J. Appl. Phys.* **95**, 1382 (2004)
3. J.H. Jeon, *J. Eur. Ceram. Soc.* **24**, 1045 (2004)
4. H.V. Alexandru, C. Berbecaru, A. Ioachim, M.I. Toacsen, M.G. Banciu, L. Nedelcu, D. Ghetu, *Mater. Sci. Eng. B.* **109**, 152 (2004)
5. H.C. Li, W.D. Si, A.D. West, X.X. Xi, *Appl. Phys. Lett.* **73**, 190 (1998)
6. W.T. Chang, L. Sengupta, *J. Appl. Phys.* **92**, 3941 (2002)
7. P.C. Joshi, M.W. Cole, *Appl. Phys. Lett.* **77**, 289 (2000)
8. L. Zhou, P.M. Vilarinho, J.L. Baptista, *J. Eur. Ceram. Soc.* **19**, 2015 (1999)
9. V.V. Lemanov, E.P. Smirnova, P.P. Syrnikov, E.A. Tarakanov, *Phys. Rev. B.*, **54**, 3151 (1996)
10. N. Baskaran, H. Chang, *Mater. Chem. Phys.* **77**, 889 (2002)
11. X.M. Chen, T. Wang, J. Li, *Mater. Sci. Eng. B.*, **113**, 117 (2004)
12. T. Mitsui, W.B. Westphal, *Phys. Rev.* **124**, 1354(1961)
13. K. Uchino, S. Nomura, *Ferroelectr. Lett. Sect.* **44**, 55 (1982)
14. J.G. Bednorz, K.A. Muller, *Phys. Rev. Lett.* **52**, 2289(1984)
15. A. Cheng, Y. Zhi, P.M. Vilarinho, J.L. Baptista, *Phys. Rev. B.* **57**, 7403(1998)
16. L. Zhou, P.M. Vilarinho, J.L. Baptista, *J. Eur. Ceram. Soc.* **21**, 531 (2001)