

EFFECT OF Sr^{2+} SUBSTITUTION ON DIELECTRIC PROPERTIES AND PTCR BEHAVIOR OF BaTiO_3

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Abstract

$\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics have been widely used as electronic materials. However, conflicting results for the effect of Sr^{2+} for the maximum value of the relative dielectric constant at the Curie point of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics have been reported. Several researchers have studied the possibility of using $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics as positive temperature coefficient resistivity (PTCR) material but complete information has not been fulfilled. The purposes of this study were to ascertain the effect of Sr^{2+} substitution on some dielectric and electrical properties of BaTiO_3 and to further investigate the possibility of utilizing $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics as PTCR materials. In this study an X-ray diffractometer and scanning microscope were used to study phases and microstructures of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$. In addition, the capacitance and resistance of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ were measured and their relative permittivity and resistivity were calculated and analyzed. Results indicated that Sr^{2+} substitutions cause the unit cell of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ to shrink and change from a tetragonal to a cubic symmetry. Moreover, Sr^{2+} substitution shifts the Curie point of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ to a lower temperature. Lastly, pure $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ does not display good PTCR characteristics for commercial PTCR material.

Keywords: BaTiO_3 , dielectric, positive temperature coefficient resistivity, PTCR

Introduction

BaTiO_3 is the most important dielectric ceramic which has been extensively studied because of its numerous applications in ferroelectric and semiconductor devices. Pure BaTiO_3 exhibits a paraelectric to ferroelectric phase transition at its Curie point at about 120 - 130°C depending on its grain size and purity (Jaffe *et al.*, 1971). It is agreed among most researchers that partial substitution of Ba^{2+} ions by Sr^{2+} ions linearly decreases the BaTiO_3 Curie temperature (Jaffe *et al.*, 1971; Jackson and Reddish, 1945; Jeon,

2004). However, conflicting results for the effect of Sr^{2+} for the maximum value of the relative dielectric constant at the Curie point of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics have been reported (Jaffe *et al.*, 1971; Liou and Chiou, 1997; Zhou *et al.*, 1999; Jeon, 2004). Zhou *et al.* (1999) showed that the maximum relative permittivity at the Curie point of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ increases with an increasing Sr^{2+} content, reaching the highest value at $x = 0.6$ and then decreases. Nevertheless, Jeon (2004) reported that the maximum

of relative dielectric constant at the Curie point of Ba_{1-x}Sr_xTiO₃ sintered at 1,400°C increases with increasing x and reaches the highest value at x=0.4.

Ba_{1-x}Sr_xTiO₃ ceramics have been widely used as a base material in the fabrication of electronic components. Theoretically, Ba_{1-x}Sr_xTiO₃ changes its resistivity at the Curie point (Haertling, 1999). Many works have been undertaken to determine the possibility of fabricating PTCR devices from Ba_{1-x}Sr_xTiO₃ ceramics (Kim, 2002; Viviani *et al.*, 2004). The purpose of this study was to ascertain the effect of Sr²⁺ substitution on the relative permittivity, Curie point, and resistivity of BaTiO₃ and to further investigate the possibility of utilizing Ba_{1-x}Sr_xTiO₃ ceramics as PTCR material.

Experimental Procedure

Specimens were prepared from 99% pure, < 5mm BaTiO₃ and SrTiO₃ powders. Powders were weighted according to the formula Ba_{1-x}Sr_xTiO₃ where x = 0, 0.1, 0.15, 0.20, and 0.25 then ball-milled for 24 h with acetone and zirconia balls in a Nalgene bottle. The mixtures were subsequently dried and mixed with 1% ww polyvinyl alcohol (PVA) solution to get 0.005 g of PVA per 1 g of powder as a binder. Next, pastes of powder and PVA solution were air-dried and crushed in a mortar and pestle to pass through a 100 mesh sieve to form granules. Afterwards, the granules were pressed under uniaxial pressure into 16 mm diameter and 2 mm thick disks. Then, green pellets were debinded at 550°C and sintered at 1,300, 1,400, and 1,420°C with the following schedule: (a) Heated from room temperature to 550°C with a heating rate of 1°C/min; (b) Held at 550°C for 2 h; (c) Heated from 550°C to sintering temperatures (1,300, 1,400 or 1,420°C) with a heating rate of 2°C/min; (d) Held at sintering temperature for 1 h; (e) Cooled from sintering temperature to 550°C with the cooling rate of 1°C/min; (f) Cooled from 550°C to room temperature at the cooling rate of 5°C/min. Sintered specimens were ground, polished and acid etched with 3% HF for 36 min. Subsequently, scanning electron microscopy (SEM) (Jeol Model

JSM6400) was used to examine the microstructures of the sintered specimens. The average grain sizes of the specimens were determined by the linear-intercept method. Phase identification of the specimens was conducted on a powder X-ray diffractometer (XRD) (Bruker Model D5005) with CuK_α radiation. The electrical properties of the specimens with Ag-Pd electrodes were measured while cooling down from 200°C to room temperature using a Hewlett Packard precision LCR meter (HP4284A) at 1 kHz frequency.

Results and Discussion

The XRD patterns for powder sintered at 1,420°C are shown in Figure 1. The results are consistent with those reported in other studies (Liou and Chiou, 1997; Jeon, 2004). It is clear from the diffraction patterns that as the Sr²⁺ substitution increases, all peaks shift to higher 2 q and the tetragonal splitting for (002)/(200) reflection pair (at 2 q about 47°) tends to be less. This result indicates that the unit cell of Ba_{1-x}Sr_xTiO₃ is getting smaller and becomes more cubic as Sr²⁺ substitution is increasing. This result could be caused by the fact that the Sr²⁺ ionic radius (1.16 Å) is smaller than the Ba²⁺ ionic radius (1.36 Å).

The density variations of sintered Ba_{1-x}Sr_xTiO₃, measured by Archimedes method, are given in Table 1. It can be seen that the densities do not vary consistently either to Sr molar fractions or sintering temperatures. However, all samples have density between 85 - 92% of the theoretical density. The SEM micrographs of specimens sintered at 1,350°C are shown in Figure 2. It is anticipated that the black area in SEM micrographs is the over-etching-region rather than pores of specimens. Because according to Table 1 the x = 0 specimen should have more pore than the x = 0.15 specimen. SEM micrographs indicate that the grain size of Ba_{1-x}Sr_xTiO₃ decreases with increasing Sr²⁺ substitutions.

Figures 3(a-b) display the temperature dependence of the relative permittivity of the Ba_{1-x}Sr_xTiO₃ ceramics sintered at 1,350°C and 1,400°C measured during cooling down at 1 kHz.

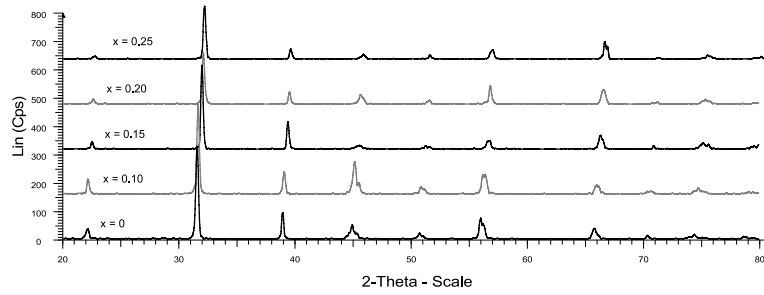
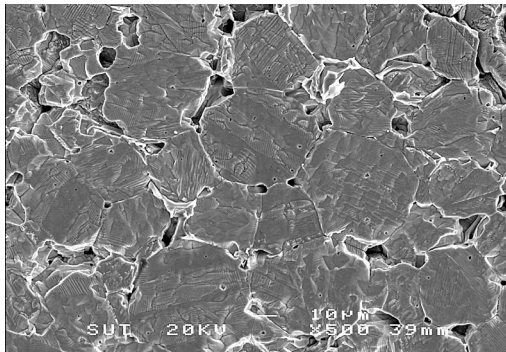
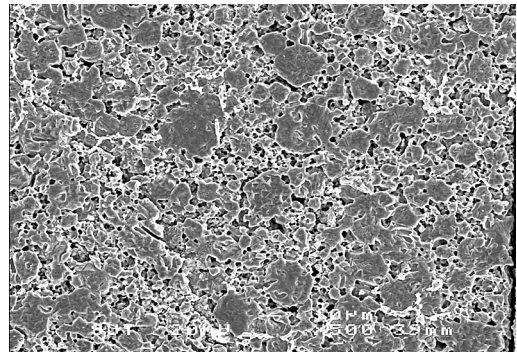


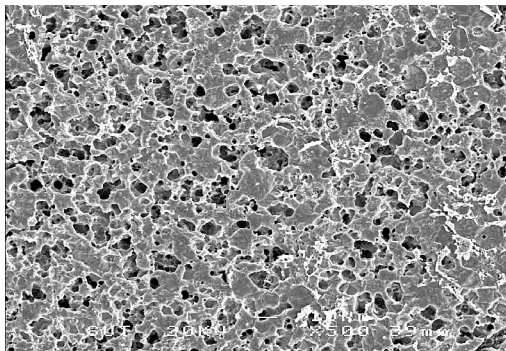
Figure 1. X-ray diffraction patterns of the sintered $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at $1,420^\circ C$ for (a) $x = 0$, (b) $x = 0.10$, (c) $x = 0.15$, (d) $x = 0.20$, and (e) $x = 0.25$



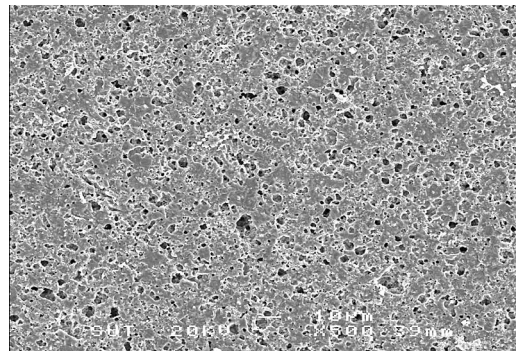
(a) $x = 0$



(b) $x = 0.10$



(c) $x = 0.15$



(d) $x = 0.20$

Figure 2. SEM Micrograph of $Ba_{1-x}Sr_xTiO_3$ polished surface specimens sintered at $1,350^\circ C$. (a) $x = 0$, (b) $x = 0.10$, (c) $x = 0.15$, and (d) $x = 0.20$

Table 1. Bulk density of the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ specimens sintered at 1,350 - 1,420 °C

Sr molar fraction (X)	Sintered at 1,350°C Bulk density (g/cm ³)	Sintered at 1,400°C Bulk density (g/cm ³)	Sintered at 1,420°C Bulk density (g/cm ³)
0.00	5.55 ± 0.05	N.A.	5.19 ± 0.05
0.10	5.40 ± 0.05	5.49 ± 0.05	5.37 ± 0.05
0.15	5.43 ± 0.05	5.34 ± 0.05	5.46 ± 0.05
0.20	5.36 ± 0.05	N.A.	5.42 ± 0.05
0.25	5.53 ± 0.05	5.12 ± 0.05	N.A.

N.A. = Not available

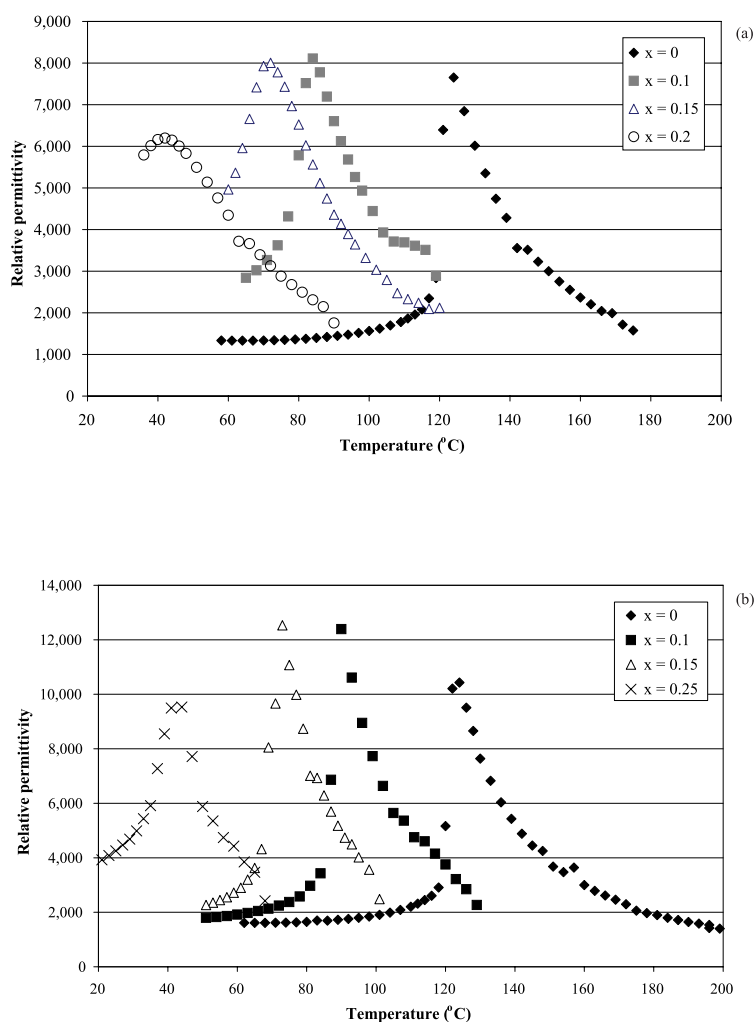


Figure 3. Relative permittivity as a function of temperature of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ sintered at (a) 1,350°C (b) 1,400°C measured during cooling from above the Curie points

The magnitude of relative permittivity in Figures 3(a-b) is comparable to those reported in the work of Jeon (2004) and Liou and Chiou (1997) work. The Curie point is defined as the temperature of maximum relative permittivity. From the figures, it can be seen that: (a) The Curie point decreases with increasing Sr^{2+} substitutions. This result is in substantial agreement with the previous findings (Jackson and Reddish, 1945; Jaffe et al., 1971; Liou and Chiou, 1997; Zhou et al., 1999; Jeon, 2004). It is interesting to note that the decrease of the Curie point is linearly related to Sr^{2+} concentration as shown in Figure 4. The equations printed on each line of Figure 4 are the best fit equations; and b) the maximum relative dielectric constant of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ increases as the Sr^{2+} mole fraction increases, reaching the highest value at about $x = 0.15$. This is quite large discrepancy from Jeon (2004) and Zhuo et al. (1999) works. According to Jeon (2004) and Zhuo et al. (1999), $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ has maximum relative permittivity at the Curie temperature when $x \approx 0.4 - 0.6$. The possible reason for this inconsistency is the difference of sample densities between this work and Jeon and Zhou's works.

Figures 5(a-b) exhibit the electrical resistivity as a function of the temperature of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ sintered at 1,350°C and 1,400°C. It can be seen that $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ changes its electrical resistivity characteristics from a negative temperature coefficient resistivity (NTCR) to a positive temperature coefficient resistivity (PTCR) at the Curie points. The room temperature electrical resistivity of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ is displayed in Figure 6. It is clear that Sr^{2+} substitution reduces the room temperature electrical resistivity of BaTiO_3 . A good PTCR material should have a high ratio of the maximum electrical resistivity to the minimum room temperature resistivity, and high capability to maintain its high electrical resistivity over the long range of temperature above its Curie point. The pure $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ samples in this experiment may not be suitable for real PTCR applications yet, but can surely be improved through optimizations and processing. Generally, good PTCR material is made by adding donor atoms to convert to $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ to be an n-type semiconductor and with a small addition of acceptor ions into its grain boundary.

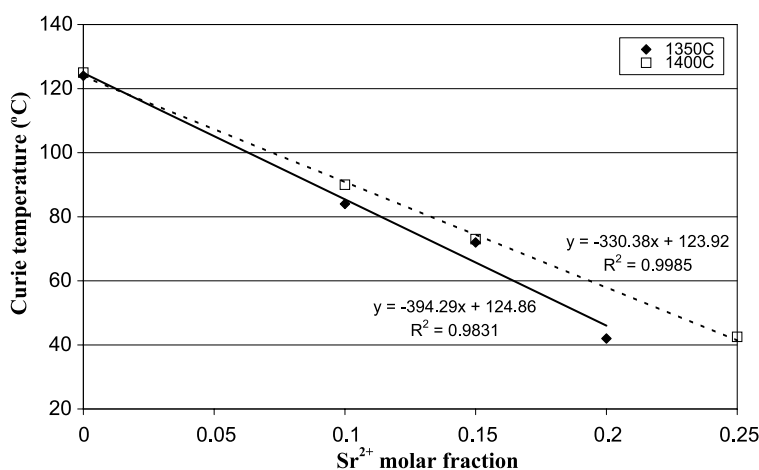


Figure 4. Curie temperature as a function of Sr molar fraction of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ sintered at 1,350°C and 1,400°C

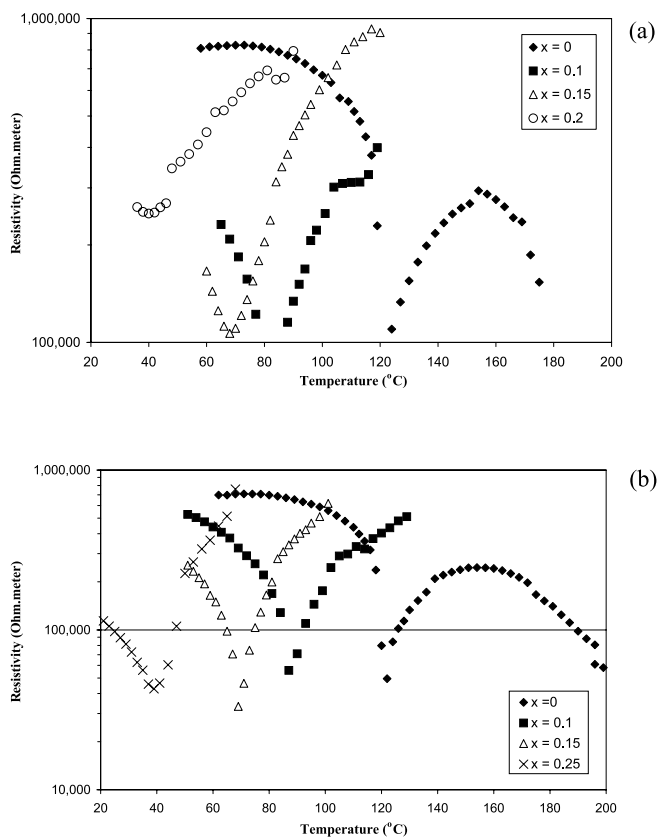


Figure 5. Electrical resistivity as a function of temperature of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ sintered at (a) 1,350°C; (b) 1,400°C measured during cooling from above the Curie points

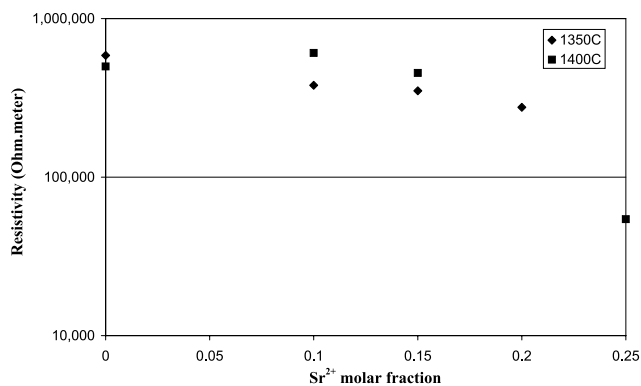


Figure 6. Room temperature electrical resistivity as a function of Sr^{2+} molar fraction of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ sintered at 1,350°C and 1,400°C

Conclusion

Sr²⁺ substitutions cause the unit cell of Ba_{1-x}Sr_xTiO₃ to shrink and change from tetragonal to cubic symmetry. In addition, Sr²⁺ addition reduces the grain size of Ba_{1-x}Sr_xTiO₃. Moreover, Sr²⁺ substitution linearly shifts the Curie point of Ba_{1-x}Sr_xTiO₃ to a lower temperature. Although pure Ba_{1-x}Sr_xTiO₃ displays PTCR characteristics when heated through its Curie point, its PTCR behavior is not good enough to be used as a commercial PTCR material. Optimization through materials selection and processing as mentioned above will surely improve these characteristics and enable this class of material to be used in real PTCR applications.

References

- Haertling, G.H. (1999). Ferroelectric ceramic: history and technology. *J. of Am. Ceram. Soc.*, 82(4):797-818.
- Jackson, W. and Reddish, W. (1945). High permittivity crystalline aggregates. *Nature*, 156(3,972):717.
- Jaffe, B., Cook, W.R., and Jaffe, H. (1971). Piezoelectric ceramics. Academic Press Ltd., India, 402p.
- Jeon, J. (2004). Effect of SrTiO₃ concentration and sintering temperature on microstructure and dielectric constant of Ba_{1-x}Sr_xTiO₃. *J Eur Ceram Soc*, 24:1,045-1,048.
- Kim, J. (2002). Synthesis of porous (Ba, Sr)TiO₃ ceramics and PTCR characteristics. *Mater. Chem. and Phys.*, 78:154-159.
- Liou, J. and Chiou B. (1997). Effect of direct-current biasing on the dielectric properties of barium strontium titanate. *J. of Am. Ceram. Soc.*, 80(12):3,093-3,099.
- Viviani, M., Leoni, M., Buscaglia, M., Buscaglia, V., and Nanni, P. (2004). Positive temperature coefficient of electrical resistivity below 150K in barium strontium titanate. *J. Am. Ceram. Soc.*, 87(4):756-58.
- Zhou, L., Vilarinho, P.M., and Baptista, J.L. (1999). Dependence of the structural and dielectric properties of Ba_{1-x}Sr_xTiO₃ ceramic solid solutions on raw material processing. *J Eur Ceram Soc*, 19:2,015-2,020.

