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Effects of zirconium on the structural and dielectric properties of (Ba, Sr)TiO_3 solid solution

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The effects of zirconium on (Ba, Sr)TiO_3 solid solution are studied by preparing $(Ba_{0.75}Sr_{0.25})(Zr_yTi_{1-y})O_3$ (BSZT) ceramics with y ranging from 0 to 0.15. With increased incorporation of zirconium the lattice parameters increase with decreasing c/a ratio, while a linear relationship is found between $(a^2c)^{1/3}$ values and the content of zirconium. The Curie temperature (T_c) is also lowered linearly with increasing y. The Curie temperature of the $(Ba_{1-x}Sr_x)(Zr_yTi_{1-y})O_3$ system can be estimated by $T_c = 125 - 270x - 350y$ (° C). Observations of microstructures also show that a small amount of zirconium promotes the grain growth, while a higher content will then inhibit it. Dielectric properties of BSZT dielectrics and BSZT-based boundary layer (BL) capacitors are also correlated to have similar temperature dependence, where the maximum dielectric constant at room temperature is found at $y = 0.1$.

1. Introduction

Barium titanate is widely used as a capacitor dielectric because of its high dielectric constant property with low dissipation factor [1, 2]. As is well known, semiconducting $BaTiO_3$ ceramics are also developed in the fabrication of grain boundary barrier layer (GBBL) capacitors [3, 4]. In order to improve the temperature coefficient of capacitance (TCC) near the Curie point, at which phase transition from tetragonal to cubic phase occurs, methods of substitutional solid solution are reported [5–9]. Hennings *et al.* reported the dielectric properties of (Ba, Ca) (Ti, Zr)O_3 solid solution [5] as well as the diffuse ferroelectric phase transition in $Ba(Ti_{1-y}Zr_y)O_3$ system [6], which has very high and broad Curie maxima and is often used for Z5U ceramic dielectrics.

Recently, Surowiak *et al.* [7] reported the $Ba(Ti_{1-x}Sn_x)O_3$ thick film and Yoon *et al.* [8] even studied the $(Ba_{0.9}Ca_{0.1})(Ti_{1-x}Sn_x)O_3$ system. All these reports are based on the substitution of Ba^{2+} or Ti^{4+} by the isovalent ions of perovskite materials having similar structurs to $BaTiO_3$. With the substitution, the Curie point of the solid solution is shifted and the phase transition is diffused.

On the other hand, ceramics based on (Ba, Sr)TiO_3 solid solutions are frequently used for T_c-controlling in PTC thermistors [9], in which the Curie point is lowered with increasing content of strontium, but no diffused phase transition is found. Dungan *et al.* [10] studied the dielectric properties of the (Ba, Sr) (Ti, Sn)O_3 system which also has broad dielectric maxima, and they concluded that the decrease of Curie temperature which results from substitution of Ti^{4+} by Sn^{4+} is about twice as effective as substitution of Ba^{2+} by Sr^{2+} in this regard. In our previous studies [11, 12], semiconducting BSZT ceramics with their applications are reported, but the effect of zirconium is not discussed. In this paper, we investigate the effects of zirconium on the (Ba, Sr)TiO_3 solid solution, including the structural properties, Curie point shift, dielectric properties and the correlation with GBBL capacitors.

2. Experimental procedures

Raw materials of $BaCO_3$, $SrCO_3$, TiO_2 and ZrO_2 (Merck, purity higher than 99.5%) are used to prepare the compositions of $(Ba_{0.75}Sr_{0.25})(Zr_yTi_{1-y})O_3$ system with $y = 0$, 0.05, 0.1 and 0.15 to study the effect of zirconium. A small amount of TiO_2 (0.2 mol %) and SiO_2 (0.2 wt %) are added to promote the sintering.

Wet ball-milling is adopted for 4 h with distilled water. After it has been dried completely, the mixed powder is calcined at 1150° C for 2 h, and then ground for pressing into disc-type samples of 14 mm in diameter. The solid-solution of the calcined powder is examined by the X-ray diffraction (XRD) analysis. Lattice parameters are calculated from the (1 0 3) and (301) plane reflections, which are usually adopted for tetragonal barium titanate [13].

Sintering is carried out for 4 h at 1390 and 1425° C, respectively. All the compositions with various zirconium content are fired together to ensure the same sintering conditions for comparions. Structural properties are investigated by XRD analysis and the scanning electron microscope (SEM) observations. In order to understand the effect of zirconium on the BSZT-based BL capacitors, the pressed samples are also sintered in a reducing atmosphere (2% H_2 + 98% N_2) to achieve the semiconducting properties, and are then diffused at 1250° C with the painted CuO into the grain boundary as the insulating composition.

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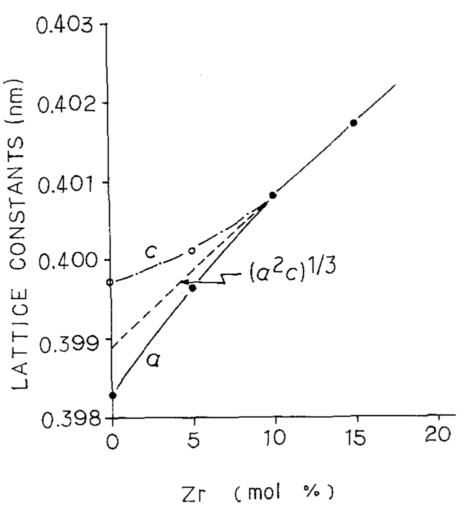

Figure 1 Variations of lattice parameters with different contents of zirconium in the $(Ba_{0.75}Sr_{0.25})$ $(Zr_yTi_{1-y})O_3$ ceramics, sintered at 1390° C for 4 h.

For dielectric property measurements, silver paste is painted on samples and fired at 700° C as electrodes. The temperature dependences of dielectric constants are measured at 1 kHz and $20\,V\,cm^{-1}$, by HP4192A LF impedance analyser. During these measurements the samples are cooled at a rate of $2°\,C\,min^{-1}$ from 100 to −20° C.

3. Results and discussion

3.1. Formation of solid-solution

Due to the similarity of crystal structures and ionic sizes, a complete series of solid-solution could be formed between $BaTiO_3$ and $SrTiO_3$ by the inter-diffusion of Ba^{2+} and Sr^{2+} ions [14, 15]. According to the observed standard enthalpies of formation of the perovskite ABO_3 structure [16], as listed in Table I, $BaTiO_3$ and $SrTiO_3$ tend to form the perovskite structures in preference to what $BaZrO_3$ and $SrZrO_3$ might do during firing the mixed reactants of $BaCO_3$, $SrCO_3$, TiO_2 and ZrO_2. Thus, $(Ba, Sr)TiO_3$ solid-solution could be formed by the proposed reactions [17]

$$BaTiO_3 + SrTiO_3 \rightarrow BaTi_xO_{2x+1} + (Ba, Sr)_2\,TiO_{4(ss)} \tag{1}$$

$$(BaTiO_3 - BaTi_xO_{2x+1})_{(liq)} + (Ba, Sr)_2TiO_{4(ss)} \rightarrow (Ba, Sr)TiO_{3(ss)} \tag{2}$$

and then, (Ba, Sr) (Ti, Zr)O_3 solid solution is formed by the incorporation of ZrO_2 as

$$(Ba, Sr)TiO_{3(ss)} + ZrO_2 \rightarrow (Ba, Sr)\,(Ti, Zr)O_{3(ss)} \tag{3}$$

TABLE I Standard enthalpies of formation of some perovskite structure titanates [16].

Perovskite structure	Calculated ($kJ\,mol^{-1}$)	Observed ($kJ\,mol^{-1}$)
$BaTiO_3$	−1500	−1650
$BaZrO_3$	−1650	−1770
$SrTiO_3$	−1540	−1680
$SrZrO_3$	−1690	−1780
$CaTiO_3$	−1580	−1660
$CaZrO_3$	−1730	−1770

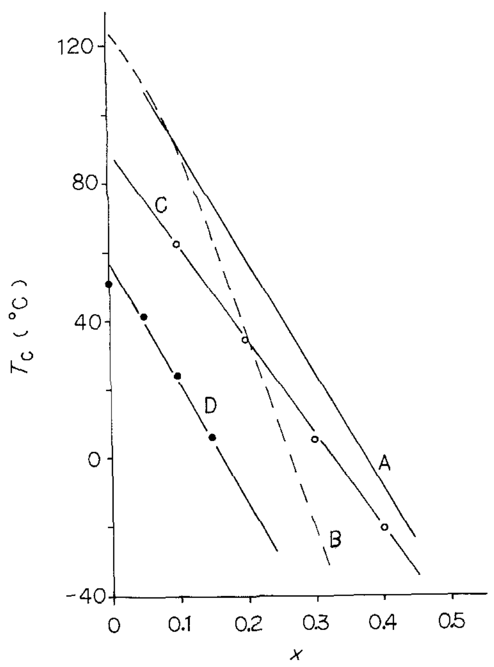

Figure 2 The curie temperatures of solid solutions with various compositions. (A: $(Ba_{1-x}Sr_x)TiO_3$; B: $Ba(Ti_{1-x}Zr_x)O_3$; C: $(Ba_{1-x}Sr_x)$ $(Ti_{0.9}Zr_{0.1})O_3$; D: $(Ba_{0.75}Sr_{0.25})$ $(Ti_{1-x}Zr_x)O_3$). The slopes for curves A [18], B [20], C, D are −3.5, −5, −2.7 and −3.5, respectively.

The XRD analysis shows there exist intermediate compounds of $Ba_6Ti_{17}O_{40}$ and $BaZrO_3$ in the calcined powder, while the XRD patterns of the sintered samples show no secondary phase except the perovskite solid-solution. This is in good agreement with the above reactions.

3.2. Lattice parameters and Curie temperature

The lattice parameters of the $(Ba, Sr)TiO_3$ solid-solutions are known to decrease monotonically from pure $BaTiO_3$ to pure $SrTiO_3$. Whereas, in the Ba(Ti, Zr)O_3 solid solution, Neirman [18] reported that the lattice constants increase with the incorporation of zirconium. The calculated lattice parameters in the $(Ba_{0.75}Sr_{0.25})$ $(Zr_yTi_{1-y})O_3$ system with y from 0 to 0.15 are depicted in Fig. 1. Both c and a increase as zirconium increased, but the c/a ratio decreases. While, a linear relationship is found between $(a^2c)^{1/3}$ and the content of zirconium. When y is higher than 0.1, c is found equal to a and the cubic phase forms. This is expected since the ionic radius of Zr^{4+} (0.087 nm) is larger than the substituted Ti^{4+} ion (0.068 nm). With increasing zirconium, the average radius of B site is expanded which leads to a faster increase of a-axis than c-axis, and the average displacement of B site ions along the polar axis is decreased which makes the tetragonal phase deformed toward cubic phase with decreasing T_c [19].

The shift of Curie temperature (T_c) with respect to the content of zirconium is plotted as curve D in Fig. 2, which is determined by the measurements of dielectric maxima. The T_c variations of $Ba(Ti_{1-x}Zr_x)O_3$ [18] and $(Ba_{1-x}Sr_x)TiO_3$ [20] are also shown in this figure for comparison. In the BSZT system, as one can find in Fig. 2, Curve B has a steeper slope than curve A, and curve D has a steeper slope than curve C. The

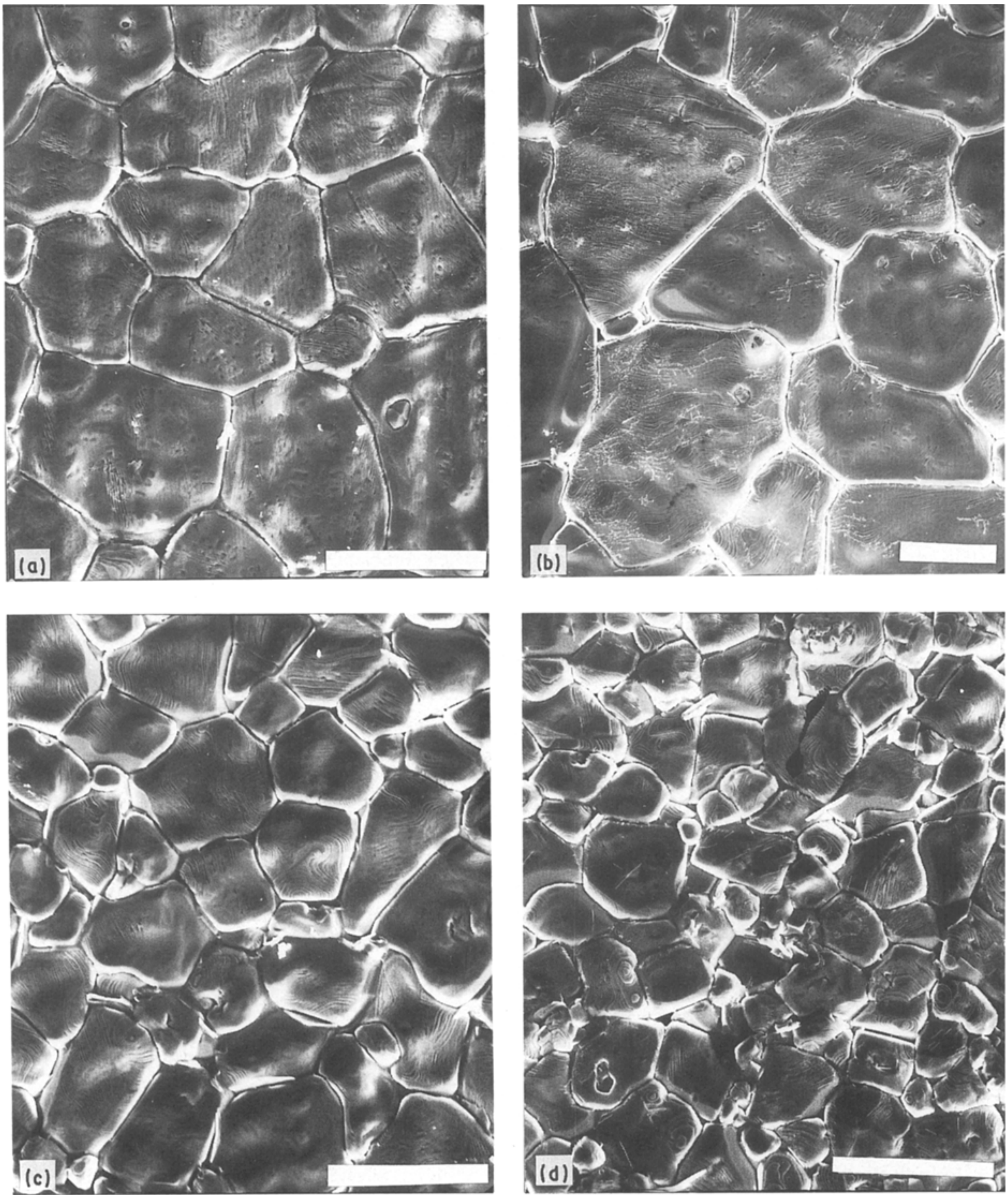

Figure 3 Microsctures of the BSZT ceramics, sintered at 1390° C for 4 h. (A) $y = 0$, (B) $y = 0.05$, (C) $y = 0.1$, (D) $y = 0.15$. (Bar = 50 μm)

decrease of T_c by substitution of Zr^{4+} for Ti^{4+} is thus more effective than that of Sr^{2+} for Ba^{2+}, similar to what is reported in the (Ba, Sr) (Ti, Sn)O_3 system [10]. The decrease of T_c with increasing strontium is explained by the increased covalent bond energy of the A–O bonding in ABO_3 structure [16]. Whereas the decrease of T_c with increasing zirconium content is believed to be due to the decrease of the pseudo Jahn–Teller effect [21], which states T_c increases with the vibronic interaction.

Since curves C and D have a shallower slope than curves A and B, this means when substitutions of both A site and B site are undertaken, the decrease of T_c is not so effective as single-site substitution of the same content. In other words, the weakened vibronic interaction and expanded unit cell due to incorporation of zirconium might compensate, to some extent, against the tendency of increasing covalent bond energy of A–O bonding, which results from substitution of Sr^{2+} for Ba^{2+} ions. With reference to the slopes of curves C and D, and assuming the T_c of $BaTiO_3$ be 125° C [18], an equation is submitted here to approach this superposition effect of Curie temperature for the $(Ba_{1-x}Sr_x)(Zr_yTi_{1-y})O_3$ solid solution

$$T_c = 125 - 270x - 350y\ (^\circ\mathrm{C}) \tag{4}$$

where x is the strontium content in the A site and y the zirconium content in the B site. From Equation 4, the calculated and the measured Curie temperatures are listed in Table II, which are found in reasonable agreement to some extent when neither x nor y is zero.

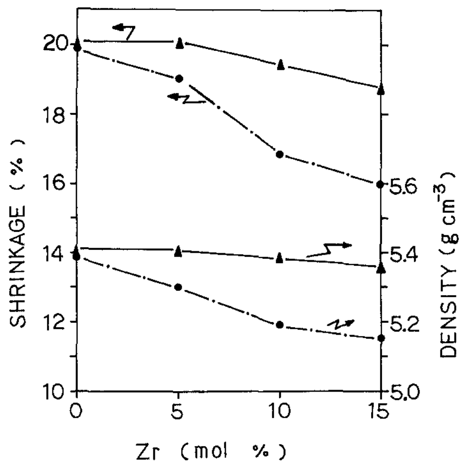

Figure 4 Shrinkage and densities of the BSZT-ceramics with y ranging from 0 to 0.15. Sintering is held at 1390° C (●) and 1425° C (▲), respectively, for 4 h.

TABLE II Comparison of measured Curie temperatures with the calculated Curie temperatures by Equation 4 for the $(Ba_xSr_{1-x})(Zr_yTi_{1-y})O_3$ system.

$(Ba_{1-x}Sr_x)$ $(Ti_{1-y}Zr_y)O_3$		Measured T_c (°C)	Calculated T_c^* (°C)	Difference $T_c - T_c^*$
x	y			
0.25	0	51	57.5	−6.5
0.25	0.05	41.5	40	1.5
0.25	0.1	23.5	22.5	1
0.25	0.15	6	5	1
0.1	0.1	61	63	−2
0.2	0.1	34	36	−2
0.3	0.1	5	9	−4
0.4	0.1	−21	−18	−3

3.3. Microstructures

Fig. 3 shows the microstructures of the samples sintered at 1390° C for 4 h. A small amount of zirconium ($y = 0.05$) is found to promote the grain growth, but for higher content of zirconium ($y = 0.1$ or higher), the increased zirconium seems to inhibit the grain growth. According to the phase diagram of TiO_2–ZrO_2 system [22], its eutectic point is lowered with small amount of ZrO_2, the enhanced grain growth found when $y = 0.05$ is thus expected to be due to liquid phase sintering, while with increasing ZrO_2, the TiO_2 to ZrO_2 ratio decreases and the grain growth is retarded.

The shrinkage and density of the BSZT ceramics under different sintering conditions are shown in Fig. 4. As can be seen, higher sintering temperatures lead to higher shrinkage and higher density. Higher content of zirconium, however, results in lower shrinkage and lower bulk density. This reveals that it needs more enthalpy for zirconium to take the B site of the perovskite structure than does titanium, and it is also the reason why higher zirconium content will inhibit the grain growth.

3.4. Dielectric properties

The variations of dielectric constant with temperature are shown in Figs 5a and 5b for sintering at 1390 and 1425° C, respectively. It can be found that with increasing incorporation of zirconium, the maximum dielectric constant increases apparently until $y = 0.1$, and then decreases with a broad peak when y is higher than 0.1. The broadened dielectric constant peak is due to the diffuse phase transition (DPT) which occurs when sufficient substitution of titanium by zirconium has been reached, and it will result in dielectric relaxation as is well known in relaxor. Since the permittivity maxima of the composition $y = 0.1$ occurs around room temperature, it has the highest dielectric constant, in comparison with other compositions, at room temperature.

If the sintering temperature is raised, as shown in Fig. 5b, the dielectric constant increases with the Curie point shifting slightly to a lower temperature. This phenomenon could be explained by the fact that higher sintering temperature will make the solid solution more homogeneous, and thus will usually have a lower Curie point temperature than the inhomogeneous solid solution of the same composition [18].

To investigate the effect of zirconium on the dielectric properties of BSZT-based BL capacitors, compositions with different zirconium content were fabricated into semiconducting ceramics by sintering in a reducing atmosphere (2% H_2 + 98% N_2), and then the CuO_2 paste painted on the surface was diffused into the grain boundaries.

Fig. 6 shows the temperature dependence of the dielectric constant for the BSZT-based BL capacitors.

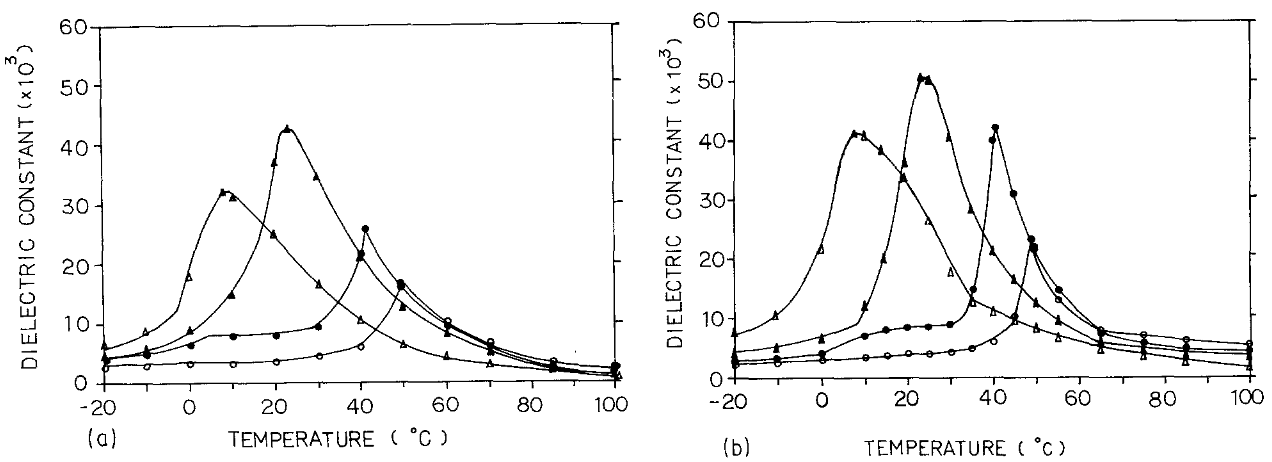

Figure 5 Temperature dependences of dielectric constant for different zirconium contents in the BSZT-ceramics. Sintering is held for 4 h at (a) 1390° C, (b) 1425° C. (△ $y = 0.15$, ▲ $y = 0.1$, ● $y = 0.05$, ○ $y = 0$)

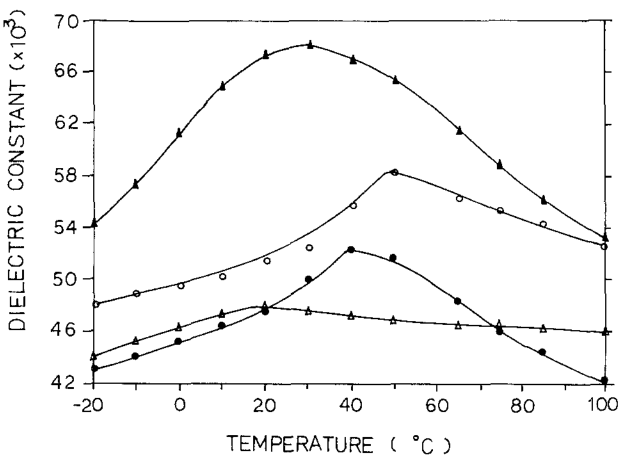

Figure 6 Temperature dependences of dielectric constant for different zirconium contents in the BSZT-based boundary layer capacitors. (△ $y = 0.15$, ▲ $y = 0.1$, ○ $y = 0$, ● $y = 0.05$).

As can easily be seen, the permittivity maximum of each composition is located at a different temperature, almost the same as that obtained in Fig. 5. This means the temperature dependences of dielectric properties of BL capacitors are mainly subjected to that of their basic compositions, but not the diffused metal oxide. From the broadened permittivity peaks, incorporation of zirconium with $y = 0.1$ will have the highest dielectric constant and can be utilized for Z5U capacitor specification. While the X7R capacitors could be obtained by increasing the incorporation of zirconium, e.g. $y = 0.15$. The improvement of the temperature coefficient of capacitance is believed to be due to the diffuse phase transition by sufficient incorporation of zirconium.

4. Conclusions

From the experimental results and discussion stated above, some effects of zirconium on the structural and dielectric properties of $(Ba, Sr)TiO_3$ solid solution are as follows.

(1) With increasing incorporation of zirconium, the lattice parameters (c and a) increase, with a linear relationship between $(a^2c)^{1/3}$ and the content of zirconium, while the c/a ratio decreases towards unity and the perovskite structure changes from tetragonal to pseudo-cubic, and then to the cubic phase.

(2) A small amount of zirconium will promote the grain growth, while more content will inhibit it. The critical content for grain growth in the $(Ba_{0.75}Sr_{0.25})(Zr_yTi_{1-y})O_3$ system should be located around $y = 0.05$.

(3) The shrinkage and densities of the sintered BSZT-ceramics decrease with zirconium addition, while the permittivity maxima increase with zirconium until $y = 0.1$, and shift to lower temperature with a broader peak.

(4) In the $(Ba_{1-x}Sr_x)(Zr_yTi_{1-y})O_3$ system, when both substitutions of A site and B site are undertaken ($x, y \neq 0$), the decrease of T_c is not so effective as single-site substitution ($x = 0$, or $y = 0$). The Curie temperature can be estimated to some extent by Equation 4.

(5) The temperature dependence of dielectric properties of the BL capacitors is mainly subjected to their composition, but not the diffused metal oxide. The incorporation of zirconium improves the temperature coefficient of capacitance due to the DPT effect.

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