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Evaluation on Structure Modification and Properties of (Ba$_{1-x}$Sr$_x$)(Ti$_{1-y}$Zr$_y$)O$_3$ Ceramics by using Rietveld Method

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1. Introduction

The BaTiO$_3$, BT, is representative ferroelectric prototype because of its excellent electrical property [Maison, 2003; Yu et al., 2004]. After the discovery of ferroelectricity in BT, research from various laboratories all over the world start studies of solid solutions of BT with other perovskites such as ATiO$_3$ and BaBO$_3$ where A=Ca, Sr, Pb, Mn and B=Zr, Sn, Hf, Mn. [Lemanov, 2007] This research field is of great basic and applied interest since the experimental results should facilitate developing of theory and fining of ferroelectric solid solutions with properties optimal for application. The phase development and dielectric behavior of various perovskite ferroelectric ceramics was reported, which may be applied to several micro- or nano-positioning devices such as deformable mirrors, microactuators, miniaturized transducers, multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices [Haertling, (1999); Uchino, (1998); Polli, (2000)].

BT has been studied extensively in solid solution with SrTiO$_3$, ST, to form a nonlinear ferroelectric with high dielectric constant ceramic Ba$_{1-x}$Sr$_x$TiO$_3$, BST, for application as integrated storage capacitors in giga bit dynamic random access memory (DRAM) due to their low dielectric loss, loss leakage current, low temperature coefficient of dielectric constant and the composition dependent Curie temperature. [Rout & Panigrahi (2006)] It is well known that these properties critically depend on their composition and structural characteristics. [Bhalla et al., (2000); Dutta et al. (1994); Wei et al. (2008), Ezhilvalavan & Tseng (2000), Carlson et al. (2000); Zimmermann et al. (2001); Loachim et al. (2007)] Formation mechanism of BST from a mixture of BT and ST had been investigated by Kolar et al. [Kolar et al. (1982)] who reported that the formation of BST was governed by preferential diffusion of Ba$^{2+}$ ion into ST. The preferential diffusion disturbs sintering in BT-ST powder mixture, whereas formation of a liquid phase results in exaggerated grain growth. In addition, two-stage sintering process was reported by Kolar et al, the similar process was also reported by Rout and Panigrahi. [Rout & Panigrahi, (2006)]
intermediate phase such as Sr$_2$TiO$_4$, SrTi$_3$O$_7$, [Rout & Panigrahi, (2006); Bera & Rout (2005)] BaTi$_{2x+1}$O$_{2x+1}$, and (Ba,Sr)$_2$TiO$_3$ [Kolar et al. (1982)] were observed or not for BST formation.

The BaTi$_{1-x}$Zr$_x$O$_3$ BTZ solid solution formed from BaTiO$_3$ and BaZrO$_3$ (BZ) has received much attention and most studies are focused on the temperature dependence of the dielectric constant, the nature of phase transition, and the relaxor behavior of this material. [Yu et al., 2002; Bera & Rout, 2005] The formation mechanism of BTZ solid solution was explored by Bera and Rout [Bera & Rout, 2005] who deduced the diffusion of BT into BZ, where the BT acts as diminishing core. Currently, BTZ has been chosen as an alternative material to replace BST in the fraction of ceramic capacitors due to the [ZrO$_6$] cluster is chemically stable than those of [TiO$_6$]. [Qin et al., 2008; Tsurumi et al., 2011; Tsurumi et al., 2011, Yu et al., 2002] The dielectric properties and phase transformation temperature, Tm (from ferroelectric to paraelectric), of BTZ are strongly dependent on Zr content into the lattice. [Badapanda et al., 2009] Yu et al. [Yu et al., 2002] had reported the dependence of Zr content on structure and dielectric properties, who also demonstrated the excellent dielectric properties were found owing to various additions of Zr into the BT lattice.

The phase formation kinetics and mechanism of SrTiO$_3$-SrZrO$_3$ (STZ) solid solution through solid-oxide reaction had reported by Bera and Rout. [Bera & Rout, 2005] They showed that the ST was formed at lower temperature of 800°C with lower activation energy of 42.274 kcal/mole than SZ. SZ formation started at 1000°C with higher activation energy of 65.78 kcal/mole. However, STZ formation started at 1500°C onward with very high activation energy of 297.52 kcal/mole. It is also concluded that the solid solution formed coherently with SZ lattice by diffusion of Ti into the SZ due to the ST plays a diminishing role and the intensity of SZ increases with the sintering temperature increasing as shown in XRD patterns.

Few lectures was reported to investigate the structure and dielectric properties of (Ba$_{1-x}$Sr$_x$)(Ti$_{1-y}$Zr$_y$)O$_3$. BSTZ, ceramics. The dielectric properties and tunability of (Ba$_{0.80}$Sr$_{0.20}$)(Ti$_{1-x}$Zr$_x$)O$_3$ multilayered thin films as a function of Zr content was reported by Wang et al. [Wang et al., 2004] The dielectric properties of (Ba$_{1-x}$Sr$_x$)(Ti$_{0.5}$Zr$_{0.5}$)O$_3$ ceramics as a function of Sr content was explored by Bera, and Rout [Bera & Rout, 2007] who showed the solid solution of (Ba$_{1-x}$Sr$_x$)(Ti$_{0.5}$Zr$_{0.5}$)O$_3$ ceramics remains cubic phase up to x<0.6 and becomes tetragonal in the range of x=0.6-1.0. However, the effect of both Sr and Zr contents on the structure and dielectric properties was not reported. In this study, the structure and dielectric properties of BSTZ ceramics were investigated as a function of both Sr and Zr contents.

2. Experimental procedure

The intermediate source ceramics of BT and BZ were separately prepared via the method of solid-state reaction. The starting materials, BaCO$_3$ (99.9 pct, Katayama, Japan), TiO$_2$ (99.9 pct, Katayama), SrCO$_3$ (99.9 pct, Katayama, Japan), and ZrO$_2$ (99.9 pct, Showa, Japan) powders with a stoichiometric composition of BaTiO$_3$, BaZrO$_3$, and SrTiO$_3$ respectively, were ball milled with deionized water for 10 h and then calcined at 1200°C for 2 h to form the single-phase BT and BZ powders. The BT and BZ powders were blended into several compositions according to the stoichiometric composition of BaZr$_x$Ti$_{3-x}$O$_9$ with $x = 0, 0.05, 0.10, and 0.15$. After drying, the binder of 1 wt% PVA was added to form a disk in size of 12 mm in diameter and 0.8-mm thickness under a pressure of 3.9 MPa. These samples were sintered at 1350°C for 1.5 h in a furnace and then cooled to room temperature. The structure
of the samples was analyzed by X-ray diffraction (D/Max V, Rigaku, Tokyo, Japan), Cu Kα (λ = 1.54056 Å) with a scanning rate ranging from 0.25 to 0.5 deg/min at a step of 0.02°. The structure model was calculated using the Rietveld method according to the XRD patterns. The microstructure of ceramics were analyzed by TEM (model 3010, JEOL), and the Ag-pasted samples were used as electrodes after being sintered at 780°C for 2 h and stabilized for 30 days. The dielectric constant of BZT was measured by using an impedance analyzer (HP4263A, Yokagawa Hewlett Packard, Tokyo, Japan) with an applied AC voltage of 1 V and a frequency of 1 kHz at temperatures ranging from -40°C to 140°C. The dielectric constant ($\varepsilon_r$) was calculated using Eq.(1):

$$\varepsilon_r = \frac{C \cdot d}{(\varepsilon_0 \cdot A)}$$  

where $C$ is the capacitance, $d$ the sample’s thickness (m), $A$ the area of Ag electrode (m²), and $\varepsilon_0$ the permittivity of the free space (8.854×10⁻¹² F/m). The hysteresis loop was measured at 10 kHz and 5 V by using a modified Sawyer–Tower circuit.

3. Results and discussion

3.1 Structure analysis

For (Ba$_{1-x}$Sr$_x$)(Ti$_{1-y}$Zr$_y$)O$_3$ ceramics preparation, the intermediate materials, BaTiO$_3$, BaZrO$_3$, and SrTiO$_3$ ceramics, were respectively prepared and sintered at various temperatures, which were analyzed by XRD to choose the co-sintering temperature at which the complete phase formation was finished. Fig. 1(a) shows the BT ceramic was formed through the reaction BaCO$_3(s)$+TiO$_2(s)$=BaTiO$_3(s)$+CO$_2(g)$ at temperature of 1000°C onward. The BZ ceramic could form through the reaction BaCO$_3(s)$+ZrO$_2(s)$=BaZrO$_3(s)$+CO$_2(g)$ at temperature of 1100°C onward as shown in Fig. 1(b). And the ST ceramic was formed through the reaction SrCO$_3(s)$+TiO$_2(s)$=SrTiO$_3(s)$+CO$_2(g)$ at temperature of 1000°C onward as shown in Fig.1(c). It suggested that the complete solid solution in BT, BZ, and ST systems was obtained at 1200°C. The activation energy for BT formation is lower than that of BZ. The BT formation started at 700°C, however, the BZ formation started at 800°C. [Bera & Rout, 2005] It is also found that the temperature of complete BZ formation is higher than BT. The ST formation is also started at temperature of 800°C with an activation energy similar to that of BZ. [Rout & Panigrahi, 2006] However, it was found that the sintering situation was similar to that of BT as shown in Figs. 1(a) and 1(c). These results demonstrate the sintering temperature of 1200°C is chosen for BSTZ ceramics sintering, which is high enough for complete solid-state reaction to form a solid solution. The reports of Rase et al. [Rase & Roy, 1955], Dry’s et al. [Dry’s & Trzebiatowski, 1957], and Kwestroo et al. [Kwestroo & Paping, 1959], the solid solutions of BaTiO$_3$, BaZrO$_3$, and SrTiO$_3$ ceramic could form completely to be the source materials of BSTZ ceramics. The formation temperature of BTZ was also reported by Bera and Rout [Bera & Rout, 2005] who pointed out the temperature is 1300°C due to loose powders and from BaCO$_3$, TiO$_2$ and ZrO$_2$. In this study, a compressed pressure of 3.0 MPa was used to form a disc for ceramics sintering. The bulk density of sintered ceramics was affected by many factors, such as sintering temperature, atomic mobility, particle size, etc. The atomic effect was investigated for ST and BZ addition in BT. Fig. 2 shows the temperature dependence of bulk densities of BT, (Ba$_{0.90}$Sr$_{0.10}$)(Ti$_{0.85}$Zr$_{0.15}$)O$_3$, and (Ba$_{0.85}$Sr$_{0.15}$)(Ti$_{0.85}$Zr$_{0.15}$)O$_3$ ceramics. It suggests two facts, one is the higher sintering temperature is needed for higher both ST and BZ additions, the other is higher temperature dependence owing to ST additions. For BST solid solution, the bulk
density decrease with the Sr content increasing although the lattice constant of BST ceramics decrease. [Muta et al., 2004] The similar trend was found by Bera and Rout [Bera & Rout, 2007] who also found the bulk density decreased and the apparent porosity increased with Sr content increasing even although the ceramics were sintered at 1600°C for 1 h. They also found that the \((\text{Ba}_{1-x}\text{Sr}_x)(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3\) ceramics remained cubic up to 50 at% substitution, only peaks were shifted towards high angle yielding the decrease in lattice parameter due to the substitution of bigger \(\text{Ba}^{2+}\) by smaller \(\text{Sr}^{2+}\) in the structure.

![Fig. 1. XRD patterns of (a) BT, (b) BZ and (c) ST as a function of sintering temperature.](image)

![Fig. 2. Dependence of bulk density on sintering temperature for various \((\text{Ba}_{1-x}\text{Sr}_x)(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3\) ceramics.](image)
The structures of BT and BTZ ceramics with various Zr substitutions were analyzed by XRD and shown in Fig. 3(a). It is suggested that no intermediate phase formed even 15% BZ was added into BT. However, the structure of BT was changed owing to the BZ addition. Hennings et al. [Hennings et al., 1982] had reported the structure changed from tetragonal to cubic phase with a lattice constant, $a$, of 4.052Å as the BZ content reached 25%. The influence of BZ addition on BT lattice constant was studied and showed in c axis reflections such as (103), (301), and (310), which was analyzed between 74° -76° as shown in Fig. 3(b). It shows that the lattice constant of BT increases with the BZ content increasing and the peaks of (310) and (301) were both merged and shifted to (103). The Zr substitution yields that the lattice constant of BTZ increase and the tetragonality decreased. Bera and Rout [Bera & Rout, 2005] had reported the larger lattice constant was obtained owing to the $\text{Zr}^{4+}$ content increasing.

Fig. 3. (a) The XRD pattern of BTZ as a function of BZ content and (b) Enlarge view in $2\theta$ of 74-76°.

The microstructure of BZT was investigated and reported in the previous study [Huang et al., 2008]. The mixture of tetragonal and cubic phases of BZT was found in the TEM analysis, which is difficult to be detected by using XRD as shown in Fig. 3(a). The bright-field (BF) and dark-field (DF) of the BZT ceramic are shown in Figs. 4(a) and 4(b), denoting grains precipitated in the matrix. The selected area electron diffraction (SAED) analyses of the $\text{Ba(Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$ crystal marked as A and B are also shown in Figs. 4(c) and 4(d).
respectively. The indexing of the SAED patterns reveals that A is a cubic phase and matrix B is a tetragonal phase, which demonstrates that the BZ content induces cubic phase formation in the matrix of the tetragonal one; this demonstrates the coexistence of both tetragonal and cubic phases in the BTZ ceramics. The result of TEM analysis demonstrates that the XRD analysis is not sensitive to second phase formation resulting that numerous false conclusions may be arrived at if the ceramic is considered as a single phase.

Hennings et al. (1982) reported that a diffuse phase transition observed near the Curie temperature of BZT ceramics is shown to be caused by coexisting ferroelectric and paraelectric phases, which can be described by a normal distribution of Curie temperatures. In addition, a small difference in the Curie temperature was observed, therefore, two reasons were deduced: a mechanical stress distribution in the material or variation in chemical composition caused by sintering process. For a BTZ solid solution formation, the substitution of Ti$^{4+}$ by Zr$^{4+}$ results in mechanical stress formed in the BZT ceramics; consequently, a lattice constant shift was detected. The mixture of BT and BZ results in the increase in entropy of BTZ ceramics. [Kamishima et al., 2008] This increase of entropy gives the decrement of Gibbs free energy. [Kamishima et al., 2008] Therefore, the coexistence of cubic and tetragonal phases of BZT is possible. Owing to the limitations of XRD, the simulation of the Rietveld method should prove to be a powerful tool both for determining the existence of the cubic phase and for reducing inaccuracies in the lattice determination.

Fig. 4. TEM analysis of Ba(Ti$_{0.85}$Zr$_{0.15}$)O$_3$: (a) BF, (b) DF, (c) SAED of A grain, and (d) SAED of B grain.

The ratio of the cubic/tetragonal phase and their lattice parameters are of utmost concern. The Rietveld method was usually used to simulate the precise structure of ceramics to determine the content of tetragonal and cubic phases. In order to obtain the exact lattice constants of BZT, the XRD patterns were measured at a very slow scanning rate (0.25 to 0.5 deg/min by a step of 0.02 deg) and calibrated with Si powders. The lattice constant and the phase ratio were calculated by Rietveld method and the results were listed in Table 1. For
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This calculation, the reliability index of the weighted profile R factor, \(R_{wp}\), values of 17.45%, 15.95%, and 17.92% were obtained, which means the simulation is reliable; in addition, the goodness-of-fit indicator, \(s\), values of 1.4, 1.1, and 1.3 were obtained, which means a good fitting is accomplished. The phase ratio changes which examined as a function of BZ content listed in Table 1, where the cubic phase in the BTZ solid solution is 36.73% for 5 mol% BZ addition. Furthermore, when the BZ content is increased to 15 mol%, the cubic phase ratio is 64.9%. The content of the cubic phase increases along with the increasing BZ content, although the increment decreases as the BZ level rising. The density of the bulk crystal estimated by the Rietveld method is very close to the measured value has been demonstrated by Souma and Ohtaki. [Souma, & Ohtaki, 2006] The higher the density, the lower the vacancy or void in the ceramics, resulting in both a higher dielectric constant and a lower Curie temperature. The dielectric behavior should be predictable, based on a combination of the existence of the cubic phase, the \(c/a\) ration of the tetragonal phase, and the theoretical density for ceramics with various BZ contents.

| Composition                  | Tetragonal phase | Cubic phase | Ratio of cubic to tetragonal phases |
|------------------------------|------------------|-------------|-----------------------------------|
| \(\text{BaTiO}_3\)           | \(a\) 3.99423, \(c\) 4.03457 | \(a\) 4.02230 | 0.00:100.0                         |
| \(\text{Ba(Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3\) | \(a\) 4.00715, \(c\) 4.02142 | \(a\) 4.02473 | 36.73:63.27                        |
| \(\text{Ba(Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3\) | \(a\) 4.02353, \(c\) 4.02906 | \(a\) 4.03765 | 56.23:43.77                        |
| \(\text{Ba(Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3\) | \(a\) 4.03943, \(c\) 4.04569 | \(a\) 4.05367 | 64.87:35.13                        |

Table 1. The lattice constants and phase ratios of cubic and tetragonal phases of BT and BTZ.

For BTZ ceramics, the relation between the tetragonality and the BZ content is shown in Fig. 5. It reveals that the tetragonality of BZT dramatically decreases (from 1.0101 to 1.0035) as the content of BZ is increased from 0 to 5 mol%, but then only slightly decreases (from 1.0035 to 1.0016) when the BZ content is increased from 5 to 15 mol%. Arlt [Arlt, 1990] has reported that the formation of the ferroelectric domain fundamentally reduces the homogeneous stress within a given grain. As this happens, the inhomogeneous stress mainly forms in the grain boundaries, where a large internal stress occurs. When the tetragonality decreases, it leads to reduced internal stress due to the formation of 90 deg ferroelectric domains resulting that the dielectric constant increases and the \(c/a\) ratio decreases to constrain spontaneous polarization. By increasing the BZ content, the tetragonality of the tetragonal phase approaches 1, and the lattice constants of \(a\) and \(c\) of the tetragonal phase come close to the lattice constant of \(a\) value of the cubic phase.

When the ST was added into the BT, the structure of BST was analyzed by XRD and shown in Fig. 6. Fig. 6(a) shows that the formation of BST ceramics without any intermediate product. The similar reflections were found for BST ceramics with the ST content in the range of 0-15 mol%. The \(\text{Ba}^{2+}\) ion was replaced by smaller radius ion of \(\text{Sr}^{2+}\) resulting in the reflection peaks shift toward higher angle. In addition, the crooked reflections of reflection peaks of BST were still maintained as shown in Fig. 4(b). In comparison with Fig. 3, the
addition of ST in A site only affects the lattice constant but little effect on the tetragonality of BT. Keller & McCarthy [Keller & McCarthy, 1982] had reported the tetragonal phase transfer completely to cubic phase with a lattice constant of 3.965 Å when the SrTiO₃ content is higher than 40%. Because the ion radius of Sr²⁺ is smaller than that of Ba²⁺, the lattice constant decreases with the ST content increasing. The Ba-rich (Baₓ₋ₓSrₓ)TiO₃ ceramics have perovskite tetragonal structure. [Remmel et al., 1999] Sr-rich (Baₓ₋ₓSrₓ)TiO₃ ceramics have perovskite cubic structure. [Izumskaya et al., 2010] The lattice constant of BST versus composition had reported by Baumert et al. [Baumert et al., 1997] who showed the cubic phase was found when the ST content is higher than 24% which is lower than that of Keller. Anyway, the perovskite tetragonal structure remains with the ST content in the range of 1-15 mol% addition.

Fig. 5. Dependence of BTZ tetragonality on BZ content.

As shown in Fig. 6(b), the tetragonal phase was still maintained with various ST additions. The lattice constant of BST was simulated by Rietveld method as single tetragonal phase and the result was listed in Table 2. It is found that the lattice constants of both a and c of BST decrease with the ST content increasing. Comparison with Ba²⁺, the ion radius of Sr²⁺ is smaller resulting that the lattice constant decreases.

Combining the effects of ZT and ST addition, the (Ba₀.₈₅Sr₀.₁₅)(Ti₀.₈₅Zr₀.₁₅)O₃ ceramics was prepared and its lattice constants was simulated as listed in Table 3. For Rietveld simulation, the best fitting result was obtained when coexistence of cubic and tetragonal phases was considered. The tetragonality of perovskite tetragonal (Ba₀.₈₅Sr₀.₁₅)(Ti₀.₈₅Zr₀.₁₅)O₃ ceramic is 1.00229 combining the enlargement and shrinkage effect of BZ and ST addition, respectively. In addition, the volume percentage of cubic phase with 43.56% was found. Comparison of Tables 1-3, the lattice constants of BSTZ ceramics are larger than BT indication the effect of Zr substitution possessing dominate role to enlarged the lattice. The tetragonality of BSTZ is also close to that of BTZ.

3.2 Dielectric properties

Fig. 7 shows the dependence of the dielectric constant of BZT and BST ceramics on the BZ and ST content, respectively. It is found that the Curie temperature decrease from 125°C to
56°C as the BZ content increase from 0 to 15%. It is found that the reduction in Curie
temperature is 4.66°C per mol% BZ addition. Masuno et al. [Masuno et al., 1972] have
pointed out that the dependence of the Curie temperature on the BZ content consistently
shows a slope of -5°C/mol%. The results are consistent with the values obtained by Masuno
et al. [Masuno et al., 1972], however, the effect of the amount of cubic phase on the dielectric
properties needs further investigation. The largest Curie temperature decrease with BZ and
ST contents is considered to be due to a decrease in the pseudo-Jahn-Teller effect. [Kristoffel &
Konsin, 1967] where the interaction between phonons and electrons results in a B-site
atom shift in a BO$_6$ octahedral structure. The interaction is reduced because the increased BZ
and ST contents and the overlap of the d$_{nn}$ and p$_{\pi}$ or bits cause the Curie temperature to
decrease. [Bersuker, 1966] It is also found that the Curie temperature decrease with ST is
larger than that with BZ. Currently, BZT has chosen as an alternative material to replace BST
in the fabrication of ceramic capacitors, since [ZrO$_6$] clusters are chemically more stable than
those of [TiO$_6$].[Badapanda et al., 2009]

![Fig. 6. (a) The XRD pattern of BTZ as a function of BZ content and (b) Enlarge view in 2θ of
74-76°.](image)

The Curie temperature of BSZT with various ZT and ST contents is higher than 50°C
indicating that the ceramics possess ferroelectric properties at room temperature. The
hysteresis loop (P vs E) of BT and (Ba$_{1-x}$Sr$_x$)(Ti$_{1-y}$Zr$_y$)O$_3$ ceramic are shown in Fig. 7 which
shows that the remnant polarization, P$_r$, may be enhanced by the addition of ZT and ST. Yu

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et al. [Yu et al., 2002] report that the $P_r$ of $\text{Ba(Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$ is 0.08 $\mu\text{C/cm}^2$, which is quite smaller, although its Curie temperature is close to room temperature. The profiles of $P$ vs $E$ are related to the crystalline structure of ceramics at room temperature. [Dixit et al., 2004] The higher the BZ content, the higher the cubic phase ratio. It could be deduced from this that the dielectric properties can be further enhanced by increasing the tetragonal phase ratio in the ceramics. The relation of $P_r$ and relative dielectric constant, $\varepsilon_r$, can be express as Eq.2:

$$P_r = \frac{1}{4\pi}(\varepsilon_r - 1)E$$  \hspace{1cm} (2)

According to the measured results as shown in Fig.7, the values of $\varepsilon_r$ were 1586, 2934, 2048, and 14340 for BT, BZT, BST and BSZT, respectively.

| Composition                  | $a$                  | $c$                  |
|------------------------------|----------------------|----------------------|
| $\text{BaTiO}_3$             | 3.99423±0.00009       | 4.03457±0.00009      |
| $(\text{Ba}_{0.95}\text{Sr}_{0.05})\text{TiO}_3$ | 3.99081±0.00008       | 4.02680±0.00009      |
| $(\text{Ba}_{0.90}\text{Sr}_{0.10})\text{TiO}_3$ | 3.98698±0.00019       | 4.01723±0.00020      |
| $(\text{Ba}_{0.85}\text{Sr}_{0.15})\text{TiO}_3$ | 3.97919±0.00018       | 4.00489±0.00019      |

Table 2. The lattice constants of tetragonal phase.

| Composition                  | Tetragonal phase $a$ | Tetragonal phase $c$ | Cubic phase $a$ | Ratio of cubic to tetragonal phases |
|------------------------------|----------------------|----------------------|-----------------|-----------------------------------|
| $(\text{Ba}_{0.85}\text{Sr}_{0.15})(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ | 4.01699±0.00030      | 4.02619±0.00036      | 4.01768±0.00015       | 43.56: 56.44                      |

Table 3. The lattice constants of $(\text{Ba}_{0.85}\text{Sr}_{0.15})(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ ceramic.

Fig. 7. Dependence of Curie temperature on BZ/ST contents.

As shown in Fig. 8, the Sr and Zr substitutions induced the $P_r$ increase in 1.5-3 times. However, the $P_r$ value of BSTZ ceramics increases dramatically for 24 times of that of BT.
is found that the restrictionism in lattice by using both Zr and Sr substitutions should yield the huge increase in dielectric properties.

Fig. 8. Hysteresis loops of (a) BaTiO$_3$, (b) Ba(Ti$_{0.85}$Zr$_{0.15}$)O$_3$, (c) (Ba$_{0.85}$Sr$_{0.15}$)TiO$_3$ and (d) (Ba$_{0.85}$Sr$_{0.15}$)(Ti$_{0.85}$Zr$_{0.15}$) (Ti$_{0.85}$Zr$_{0.15}$).

4. Conclusions

The structure of BaTiO$_3$ ceramics was modified by both SrTiO$_3$ and BaZrO$_3$ additions. Substitution with Sr in A site, the lattice constants of BST ceramics decrease but the tetragonality increases from 1.01010 to 1.05617 for 0-15 mol% addition. The remnant polarization, Pr, value increases for 1.5 times. Substitution with Zr in B site, the lattice constant of BTZ ceramics increase but the tetragonality decreases to 1.00155 for 15 mol% addition. The Pr also increases for 3 times. Substitutions of both Sr and Zr in both A and B sites, the lattice constants of BSTZ ceramics are still larger than that of BT indicating Zr substitution possessing dominate role, and the tetragonality of decreases to 1.00229 close to that of BTZ ceramics. Under these effects of both enlargement and shrinkage, the Pr dramatically increases for 24 times. It is concluded that the substitutions Sr and Zr in both A and B sites should increase effectively the dielectric properties of BSTZ ceramics.

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