Sintering Mechanism and Enhanced Piezoelectric and Crystal Structural Properties of (1-x)Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃ Lead Free Ceramics

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Sintering Mechanism And Enhanced Piezoelectric And Crystal Structural Properties Of (1-X)Ba(Zr_{0.2}Ti_{0.8})O₃-X(Ba_{0.7}Ca_{0.3})TiO₃ Lead Free Ceramics

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Featured Application: Providing method to optimize the piezoelectric

Abstract: As an lead-free piezoelectric ceramic of (1-x)Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃(here after (1-x)BZT-xBCT) has been investigated for functional devices applications. To employ as piezoelectric functional devices applications, lead-free materials with high piezoelectric charge coefficient and voltage coefficient can be indispensable for industrial applications. Piezoelectric ceramic specimens tend to shrink their size in the sintering process without melting. We focused on this phenomenon as a unique characteristic of piezoelectric ceramic materials and derived activation energy from this phenomenon using Arrhenius equation. Then associate this activation energy with piezoelectric and crystalline properties varied by sintering temperature and chemical stoichiometric composition. Piezoelectric properties can be changed depending on the sintering temperature and process conditions. (1-x)BZT-xBCT ceramics showed the highest piezoelectric coefficient of 470 pC/N. Crystalline properties and piezoelectric properties can be influenced by the sintering temperature and holding times. In this research, sintering temperature dependent structural and dielectric properties were investigated. Sintering temperature dependent shrinkage rate and activation energy were estimated and calculated for the various sintering process. In this research, two different activation energies for the shrinkage process were estimated

Keywords: Piezoelectric material, (1-x)Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃, Shrinkage mechanism, Activation energy

1. Introduction

Lead-based piezoelectric materials have been intensively investigated for their excellent piezoelectric (pC/N) and inverse piezoelectric (pm/V) properties. As a representative piezoelectric material, (Pb,Zr)TiO₃ has been extensively employed for industrial applications due to their excellent piezoelectric and mechanical properties with high Curie temperature.[1] Therefore, this material has been tested for various applications including actuators, sensors and transducers, which can be employed under heavy load and mechanical force conditions. Despite of these excellent mechanical and piezoelectric properties lead based piezoelectric materials have been faced environmental issues for toxic and harmful properties come from lead. To avoid these environmental problems, lead free alternatives have been widely and intensively investigated to replace lead-based piezoelectric materials. Among them (Bi,Na)TiO₃ (BNT), (Na,K)NbO₃ (NKN) and BaTiO₃ (BT) are the representative for lead-free piezoelectric materials. NKN have high piezoelectric charge coefficient of 160 pC/N with high Curie

temperature of 420°C. [2] But NKN has draw back of high volatile properties of Na and K due to their low melting temperature.[3] Another alternative lead-free piezoelectric material candidate, BNT, have very high piezoelectric charge coefficient 230.8 pC/N, higher electromechanical couple factor, larger remanent polarization and a better P - E hysteresis loop at relatively high temperature then other lead free piezoelectric ceramics.[4] However, open stress vs strain curve means accumulation of applied energies for lower reliability and high fatigues.[5] For the BT case, BT showed promising properties such as high piezoelectric charge coefficient more than 460 pC/N but the Curie temperature is relatively low (120°C) to employ in the industrial applications.[6-7] That is the main reason for the strict limit of BT applications. Therefore, in this research substitution type of BT material was selected to investigate the relevance between activation energy and piezoelectric properties. From the point of view of piezoelectric and dielectric properties, piezoelectric ceramics have typically been fabricated as dense in order to achieve a high d_{33} and reliable mechanical stability. In this paper, We derived the activation energy of BZT-BCT from shrinking behavior during sintering process and optimized the sintering temperature and variation of BCT contents($0.4 \leq x \leq 0.5$). We adopted the Arrhenius equation as a method to derive activation energy from shrinking behavior. $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ is intensively investigated in sensors, energy harvester applications due to their high performance of piezoelectric properties.[17,18] It has been reported that high piezoelectric charge coefficient d_{33} of 620 pC/N with curie temperature of 93°C were obtained, $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (hereafter BZT-BCT) piezoelectric ceramics have been investigated to replace lead based piezoelectric material of PZT.[12] Moreover, important feature of BZT-BCT is that R-T phase transition is expected between BCT contents of $0.4 \leq x \leq 0.5$. It has known that the existence of phase transition leads to high piezoelectric performance such as PZT and PMN-PT[12,15,16] In this study, we have focused on $(1-x)\text{BZT}-x\text{BCT}$ materials with $x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ contents of $x = 0.4, 0.425, 0.45, 0.475, 0.5$ and sintering temperature of 1475°C, 1500°C, and 1525 °C. We have been focused on the shrinkage mechanism and activation energy of BZT-BCT ceramics to explain its outstanding piezoelectric properties. We also measured the densification behavior of BZT-BCT and its microscopic surface.

2. Materials and Methods

2.1. Fabrication process of $(1-x)\text{BZT}-x\text{BCT}$

At first, stoichiometric of $(1-x)\text{BZT}-x\text{BCT}$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramic were sintered by conventional solid state sintering process. Powders of BaCO_3 , TiO_2 , ZrO_2 , and CaCO_3 were mixed with ethyl alcohol and ball milled for 24h. After the drying process, the powders of $(1-x)\text{BZT}-x\text{BCT}$ ceramics were calcined at 1350°C for 2h. Calcination process is essential because of elimination of un-desired substances such as carbides. After the calcination process, partly connected powders were smashed and re-powdered again to enhance the crystallization quality during the sintering process. Sintering process can be done to make crystalline structure. Even though, these two processes have different purpose, some processing temperature range can be overlapped. However, the calcined powders were re-powdered before the sintering process, we believe calcination process cannot affect sintering process seriously. Therefore, we believe that calcination process do not affects to derive the activation energy from Shrinking behavior. Green bodies were pressed in to disks under 3 metric tons(12mm in diameter and 1.6mm in thickness). To investigate the shrinkage mechanism of $(1-x)\text{BZT}-x\text{BCT}$ ceramics, Specimens were sintered at various temperature range of 800°C - 1525°C for holding time of 3 h with heating rate and cooling rate of 3 °C/min.[13,14]. Relative shrink ratios were measured by hydrometer and samples were thermally etched for 10 min to investigate the surface morphologies of $(1-x)\text{BZT}-x\text{BCT}$ by field emission scanning electron micrographs. Crystalline structure of $(1-x)\text{BZT}-x\text{BCT}$ ceramics were investigated by X-ray diffraction (D8-Advance/Bruker-AXS) analysis (θ - 2θ scans with Cu-K α source). The relative dielectric constant (ϵ_r) was measured by impedance analyzer (Agilent 4294A). The piezoelectric constant (d_{33}) was measured by Berlincourt type quasi-static meter. Shrinkage test of each of these samples were thoroughly measured at various sintering temperature respectively.

2.2 Mathematical method; Arrhenius equation

We , at first, plot the kinetic equation which is relative shrinkage ratio with exponent n versus reciprocal of T to derive the relation between shrinkage ratio and activation energy in equation (1). Where, L is the volume after sintering process, and L_0 is the volume before sintering process. K is the rate of constant and T is the absolute temperature.

$$\left(\frac{L-L_0}{L_0}\right)^n = \frac{Kt}{T}, \quad (1)$$

Then replot the equation as below Eq. (2) to get exponent n. In this replotted equation, t is holding time of the sintering process.

$$\ln\left(\frac{L-L_0}{L_0}\right) = \frac{1}{n} \ln\left(\frac{K}{T}\right) + \frac{1}{n} \ln(t), \quad (2)$$

Eq. (3) can be obtained from Eq.(1) as a arrhenius equation form by differentiated with respect to the T where a is the heating rate.

$$\frac{d\left(\frac{L-L_0}{L_0}\right)}{dT} = \frac{1}{n} T^{-1} a^{-\frac{1}{n}} \cdot K^{\frac{1}{n}}, \quad (3)$$

K can be rearranged by relationship between activation enegy Q, gas constant R ($R = 8.314 \text{ J/Kmol}$).

$$K = K_0 e^{-\frac{Q}{RT}}, \quad (4)$$

By rearranging Equation (1), Equation (3) and Equation (4), the following Equation (5) can be obtained

$$\ln\left\{T \left[\frac{d(L-L_0)/L_0}{dT}\right]\right\} = \ln\left(\frac{1}{n} \cdot K_0^{\frac{1}{n}}\right) - \frac{1}{n} \ln(a) - \frac{Q}{nRT}, \quad (5)$$

3. Results and Discussion

Figure 1 shows the relative shrinkage ratio of the (1-x)BZT-xBCT ceramics($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered from temperature of 800°C to 1525°C. As shown in figure, porosity of ceramic can be decreased while sintering process is proceed without melting. After the sintering process, the relative shrinkage ratio of the (1-x)BZT-xBCT ceramics($x = 0.4, 0.425, 0.45, 0.475, 0.5$) were measured. As shown in the figure 1, (1-x)BZT-xBCT ceramics started to shrinkage at 1200 °C The BCT content of 0.5 shows the highest shrinkage ratio at the temperature range of 800°C -1200°C and BCT content of 0.475 shows the highest shrinkage ratio at the temperature range of 1200°C - 1525°C. The sintering process of (1-x)BZT-xBCT ceramics was finished at near 1500 °C. Shrinkage rate of (1-x)BZT-xBCT was around 31.1 % - 34.2 % at sintering temperature of 1500 °C.

Figure 1. Relative shrinkage ratio of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for different sintering temperature.

Figure 2 shows the isothermal shrinkage curves of $(1-x)\text{BZT}-x\text{BCT}$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) depending on holding time. Different holding times were analyzed by employing the kinetic equation.[9-10]

Figure 2. Isothermal shrinkage curves of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) depending on the holding time

Also, different sintering time depending on the sintering temperature was carried out.

Eq. (2) was employed to plot the $\ln\left(\frac{L-L_0}{L_0}\right)$ vs $\ln(t)$ data depending on the holding time. The exponent of n can be calculated from the slopes ($1/n$) of the straight line fitted by the isothermal shrinkage in Figure 2. n can be related with material properties with different shrinkage rates of sintering materials. As a result, the values of n are 7.83, 7.94, 8.01, 7.94 and 8.21 for the of $(1-x)\text{BZT}-x\text{BCT}$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$), respectively. Different exponent n represents that each specimens has distinguished shrinking behavior, also leads to having their own distinct activation energy.

Figure 3 shows the activation energy of $(1-x)\text{BZT}-x\text{BCT}$ ceramics simulated by temperature dependent shrinkage rate come from figure 1. Figure 3 shows the reconstructed curves for the relative shrinkage ratio of $(1-x)\text{BZT}-x\text{BCT}$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered at 800°C to 1525°C which is translated to Arrhenius equation form. Inverse temperature versus shrinkage rate can gives activation energy from the slope of figure 1.

Figure 3. Reconstructed curves for the relative shrinkage ratio $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered from 800 to 1525 °C

As a result, from the slope (Q / nRT) of the $\ln T[\frac{d(L-L_0)}{L_0}/dT]$ versus $1/T$ equation, the activation energy for the sintering process can be calculated from the slope of Figure 2.

As shown in the figure 3, it shows that two different fitted slopes. It indicates that $(1-x)\text{BZT}-x\text{BCT}$ ceramics have two different shrinkage mechanism in temperature range 800°C -1200°C, 1200°C -1525°C, evidently. The calculated activation energies Q of temperature range of 800°C -1200°C were around 238.9, 259.4, 129.8, 141.2 and 153.58 kJ/mol, and activation energies Q of temperature range 1200°C -1525°C were around 404.9, 320.8, 276.3, 248.2 and 270.9 kJ/mol, respectively.

Table 1 lists the exponents of n and activation energies Q for $(1-x)\text{BZT}-x\text{BCT}$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$). The lowest n values is 7.83 for 0.6BZT-0.4BCT ceramics. The lowest activation energy Q of temperature range 800°C – 1200 °C is 129.8 kJ/mol for 0.55BZT-0.45BCT ceramics, and the lowest activation energy Q of temperature range of 1200°C – 1525 °C is 248.2 kJ/mol for 0.525BZT-0.475BCT. By increasing the BCT contents of $x = 0.45$ at temperature range of 800- 1200 °C, and BCT contents of $x = 0.475$ at temperature range of 1200 – 1525 °C, required minimum activation energy Q for the sintering process, respectively. Activation energy for specimens means required internal energy to grow grain during the sintering process. Therefore, the lowest activation energy leads to easily sintered compared with other specimens. [9-11]

Table 1. The values of n and the activation energy Q .

BCT[x]		0.4	0.425	0.45	0.475	0.5
n		7.83	7.94	8.01	7.94	8.21
Q[kJ /mol]	800~1200[°C]	238.91	259.43	129.86	141.26	153.58

1200~1525[°C]	404.91	320.82	276.36	248.21	270.98
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Fig. 4 shows the X-ray diffraction θ - 2θ patterns of $(1-x)\text{BZT}-x\text{BCT}$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics to know the crystalline properties sintered at 1500°C . The patterns shows that all the specimens are single-phase. BCT contents of $0.4 \leq x \leq 0.45$ showed the rhombohedral structure. As shown in the figure, the split peak of (002)/(200) at BCT contents(x) of $0.475 \leq x \leq 0.5$ indicate tetragonal structure which is phase transition region of rhombohedral phase to tetragonal phase. [16] Moreover, the Bragg reflections of the (002)/(200) planes shows that the position of the (002) peak shifted to a slightly lower angel when the BCT content was increased from 0.4 to 0.475, then shifted to higher angle at BCT content of 0.5. The position of the (002) peak at 45.02° implies relative to that that the lattice constant c of the 0.525 BZT–0.475BCT increased relative to that of other specimen. In fact, the 0.525 BZT–0.475BCT had the highest c lattice parameter among the specimens.

Figure 4. X-ray diffraction patterns of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$)

Figure 5 shows enlarged X-ray diffraction pattern, angle range of 43 to 46.5° , where (002) and (200) plane exist. Symetric shape near $2\theta = 45^\circ$ which is BCT contents of $0.4 \leq x \leq 0.45$ indicate that single Rhombohedral structure, while, Split peak of (002)/(200) plane indicate that BCT contents of $0.475, 0.5$ have Rhombohedral with tetragonal structure. It displays the peak shift of (002) of $(1-x)\text{BZT}-x\text{BCT}$ ceramics. As shown in the figure, when the composition of $x = 0.4, 0.425, 0.45$, and 0.475 , the peak positions were very similar. However, the BCT contents became 0.5 , then the (002) peak was shifted to the higher angle as composition of BCT was increased. This increased (002) peaks means that decreased lattice parameters by Bragg's law. Also, 0.525BZT–0.475BCT shows the split peak at (002) and (200) plane, meaning that increased tetragonality.

Figure 5. Enlarged X-ray diffraction patterns (002) and (200) plane of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$).

Fig. 6 shows relative density of $(1-x)\text{BZT-BCT}$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered at 1475°C, 1500°C, 1525°C. All sintering temperature shows that relative density is increasing up to BCT contents about $x = 0.475$ with 94.4% and then decreased. We believe that this increased density came from the optimized BCT contents and sintering temperature. Moreover, this bulk density probably related with morphotropic phase boundary (MPB) range near tetragonal and rhombohedral region. By stacking the uniform structure of tetragonal, bulk density can be increased.

Figure 6. Relative density of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1475, 1500, 1525 °C

Fig. 7 shows Field emission scanning electron microscopy micrographs of the thermally etched $(1-x)\text{BZT}-x\text{BCT}$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered at 1500 °C. The $(1-x)\text{BZT}-x\text{BCT}$ ceramic has an average grain size of 9.5-11 μm . As we can see in Fig 7(a), 0.6BZT–0.4BCT shows porous morphological surface, explaining the lower piezoelectric charge coefficient. With increasing BCT content, grain size is getting to larger and having a clear grain boundary, supporting the data of figure 6, bulk density of $(1-x)\text{BZT}-x\text{BCT}$ ceramics. We assumed that 0.525BZT–0.475BCT needs minimum activation energy to grow the grain, 201.88kJ/mol ,at temperature range of 1200°C - 1525°C, causing dense, fine-grain microstructure, while 0.6BZT–0.4BCT need the highest activation energy, 561.6468kJ/mol, at temperature range of 1200°C - 1525°C, causing coarse, porous-grain microstructure.

Figure 7. Field Emission Scanning Electron Microscopy micrographs of the $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1500°C

Figure 8 displays piezoelectric charge coefficient of $(1-x)\text{BZT}-x\text{BCT}$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered at 1475°C , 1500°C , 1525°C . As shown in the figure, All specimens have a tendency of increasing piezoelectric charge coefficient up to 470 pC/N at BCT content of 0.475 , and then decreased. We assumed that this high piezoelectric charge coefficient probably come from the high bulk density and MPB region of BCT contents. [12] Among other sintering temperature, sintering temperature of 1500°C specimens shows the relatively higher piezoelectric charge constant, meaning that optimized sintering temperature is 1500°C at the view of energy harvesting.

Figure

8. Piezoelectric charge coefficient of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1475°C, 1500 °C, 1525°C

Fig. 9 (a) displays dielectric constant of $(1-x)\text{BZT}-x\text{BCT}$ at 1kHz (1475°C, 1500 °C, 1525°C). Samples with all sintering conditions showed the lowest dielectric constant with BCT contents of 0.425. Then increased with the increasing BCT contents. The lowest dielectric constant of $(1-x)\text{BZT}-x\text{BCT}$ was 2431.95 sintered at 1500°C. Fig. 9 (b) displays the piezoelectric voltage constant of $(1-x)\text{BZT}-x\text{BCT}$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics at 1kHz (1475°C, 1500 °C, 1525°C). Due to relatively higher piezoelectric charge constant of sintering temperature of 1500°C specimens then other sintering temperature specimen, it shows the highest piezoelectric voltage constant. Also, BCT content of 0.475 specimen has a highest piezoelectric voltage constant in all sintering temperature condition. The highest value is 19.34 mVm/N at BCT contents of 0.475

Figure 9. (a) Dielectric constant and (b) Piezoelectric Voltage constant coefficient of $(1-x)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3-x\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1475 °C , 1500 °C, 1525 °C at 1 kHz

4. Conclusions

In this research, shrinking behavior for activation energy and piezoelectric properties of lead-free piezoelectric material $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics has been investigated. There were two shrinkage mechanisms which were located at temperature range of 800°C -1200°C and 1200°C -1525°C. Each Specimens have distinct shrinkage mechanism defined by exponent n . Among the specimens, BCT contents of 0.4 have a lowest value of exponent n , 7.83. With increasing BCT contents up to 0.475, n value and activation energy were decreased. 0.55BZT-0.45BCT shows the lowest activation energy of 129.86kJ/mol at temperature range of 800°C -1200°C and 0.525BZT-0.475BCT shows the lowest activation energy of 248.21kJ/mol at temperature range of 1200°C -1525°C. Also, low BCT content specimen have coarse-porous morphological surface and with increasing BCT contents, morphological surface became dense and fine grain structure. During the investigation of shrinkage mechanism, sintering temperature and piezoelectric properties were optimized. The $(1-x)\text{BZT}-x\text{BCT}$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered at 1500°C exhibited a relatively high bulk density compared to that sintered at other temperature. At the sintering temperature of 1500°C and BCT content of 0.475, the highest piezoelectric charge coefficient(470 pC/N) and piezoelectric voltage coefficient(19.34 mVm/N) at a frequency of 1kHz were obtained.

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Figures

Figure 1

Relative shrinkage ratio of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for different sintering temperature.

Figure 2

Isothermal shrinkage curves of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) depending on the holding time

Figure 3

Reconstructed curves for the relative shrinkage ratio $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) sintered from 800 to 1525 °C

Figure 4

X-ray diffraction patterns of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics ($x = 0.4, 0.425, 0.45, 0.475, 0.5$)

Figure 5

Enlarged X-ray diffraction patterns (002) and (200) plane of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$).

Figure 6

Relative density of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1475, 1500, 1525 °C

Figure 7

Field Emission Scanning Electron Microscopy micrographs of the $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1500°C

Figure 8

Piezoelectric charge coefficient of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1475°C, 1500 °C, 1525°C

Figure 9

(a) Dielectric constant and (b) Piezoelectric Voltage constant coefficient of $(1-x)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ - $x\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ($x = 0.4, 0.425, 0.45, 0.475, 0.5$) ceramics for sintering temperature of 1475 °C , 1500 °C, 1525 °C at 1 kHz