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Electrical Properties of (Ba,Ca)(Ti,Zr)O_3 Ceramics for Bimorph-type Piezoelectric Actuator

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In this study, lead-free $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics and a bimorph-type piezoelectric actuator were fabricated using the normal oxide-mixed sintering method, and their dielectric properties, microstructure, and displacement properties were investigated. From the results of X-ray diffraction, the pattern of the specimen has a pure perovskite structure. In addition, no secondary impurity phases were found. The excellent piezoelectric coefficient of d_{33} =454 pC/N, the electromechanical coupling factor k_p =0.51, the dielectric constant ε_r =3,657, the mechanical quality factor Q_m =239, and T_c(Tetragonal-Cubic) =90℃ were shown at x= 0.085. $\Delta k_p/k_p$20℃ and $\Delta f_r/f_r$20℃ showed the maximum value of -0.255 and 0.111 at -20℃ and 80℃, respectively. The maximum total-displacement was 60 μm under the input voltage of 50 V. As a result, it is considered that lead-free $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics is a promising candidate for piezoelectric actuator application for x= 0.085.

Keywords: BCTZ, Bimorph-type piezoelectric actuator, Piezoelectric properties, d_{33}, Lead-free

1. INTRODUCTION

Since development in the electronics industry depends on the popularity of handheld mobile devices, piezoelectric ceramics are widely used. In particular, Pb(Zr,Ti)O_3-based piezoelectric ceramics have been widely used in many application devices such as resonators, AE sensors, actuators, high-power transducers, and energy-harvesters, due to their excellent piezoelectric and electrical characteristics [1-7]. However, these Pb(Zr,Ti)O_3-based piezoelectric ceramics contain a PbO content of more than 60wt%. Consequently, lead-based piezoelectric ceramics can cause serious lead pollution, environmental problems, and human damage because of the high toxicity and high volatility of lead oxide during the manufacturing process. Also, It is very difficult to reproduce ceramics due to the alteration in the composition, owing to PbO volatilization at more than 1,000℃ [6,7]. Therefore, many researches have been extensively carried out to develop lead-free ceramics with excellent piezoelectric properties to replace the lead-based piezoelectric ceramics. Due to their excellent electrical properties over the past few years, considerable attention has been given to perovskite type lead-free ceramics such as the (Na,K)NbO_3(NKN) system, the (Bi,Na)TiO_3(BNT) system, and $BaTiO_3$(BT) system. Among these, two types of lead-free (Na,K)NbO_3 and $BaTiO_3$ ceramics have been considered as promising candidates on account of their outstanding piezoelectric properties. In 2004, Saito et al. reported on (Na,K)NbO_3 ceramics due to their high Curie temperatures(= 420℃) and excellent ferroelectric properties [8,10]. However, it is very difficult to obtain fully densified ceramics because of the high volatility of alkaline elements at high temperature sintering [10-12]. Also, $BaTiO_3$ lead-free ceramics have been given much attention since 2009, when Liu and Ren reported that the piezoelectric d_{33} constant of 620 pC/N was obtained with $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ ceramics [9,11]. However, the optimal composition of ceramics with a high d_{33} value has a low Curie temperature (T_c) and large temperature dependent degradation in the common usage temperature range. It has been known that $BaTiO_3$ ceramics can be sintered at high temperature of > 1,540℃ [13-17]. Accordingly, many difficulties arise with commercialization. To solve this problem, in order to improve the

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low Curie temperature and the temperature dependence of the piezoelectric properties, various methods such as substitution or the addition of an impurity have been proposed for these ceramics. In the present work, $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Ca_x)O_3$ lead-free piezoelectric ceramics were synthesized using the conventional solid state reaction method and the dielectric and piezoelectric properties of the ceramics were investigated. Also, the bimorph-type actuator using the $(Ba_{0.85}Ca_{0.15})(Ti_{0.915}Zr_{0.085})O_3$ ceramics was manufactured, and the total-displacement properties were then investigated.

2. EXPERIMENT

2.1 Manufacture of ceramics specimens

The ceramic specimens were manufactured using the following composition formula.

$$(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3 + 0.04\ CuO \quad (x= 0.08, 0.085, 0.10)$$

Lead-free piezoelectric ceramics were prepared using the traditional solid state method. $BaCO_3$(99%), $CaCO_3$(99%), TiO_2(99%), ZrO_2(99%), and CuO(99%) powders were used as raw materials. The powders were weighed and mixed by ball milling with ZrO_2 balls for 24 h using acetone and the mixed raw materials were then dried at 80℃. After drying, they were calcined at 1,200℃ for 2 h, the calcined powders was ball milled again with CuO and dried again. The mixed powders using PVA as a binder were sieved, and pressed into 17 φmm diameter disks at 15 MPa. After burning out the PVA, the specimens were sintered at 1,430℃ for 5h in air. The specimens were polished to 1mm thickness and then electrode posited with Ag paste. Poling was carried out at room temperature in a DC electric field of 3 kV/mm for 30 min. Bulk densities were measured with the Archimedes method using distilled water. The crystallographic study was confirmed by X-ray diffraction (XRD) using Cu Kα(λ= 1.5406 Å) radiation. The surface morphology of the ceramics was studied using a scanning electron microscope (SEM). The piezoelectric properties were measured with the resonance-antiresonance method using an impedance analyzer (Agilent 4294A). The temperature dependence of the dielectric constant of the ceramics was examined using an LCR meter (ANDO AG 4304). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter.

2.2 Measurement of the displacement of the piezoelectric actuator

Figure 1 shows the specification of the bimorph-type piezoelectric actuator. Actually, It is difficult to identify the vibration displacement of the manufactured actuator with the naked eye. Therefore, the maximized vibration of the piezoelectric actuator is identified by measuring the vibration displacement using a displacement sensor. The samples were sintered at 1,430℃ for 5 h in air. After sintering, the sintered specimen was cut to the size of 30 mm × 3 mm × 0.5 mm and was then electrodeposited with Ag paste. Poling was carried out at room temperature under a DC electric field of 3 kV/mm for 30 min. A brass plate was placed between two polarized specimens using epoxy to form the bimorph-type piezoelectric actuator. The total-displacement under the support of both ends of the bimorph was measured using a displacement sensor (ILD1700-2).

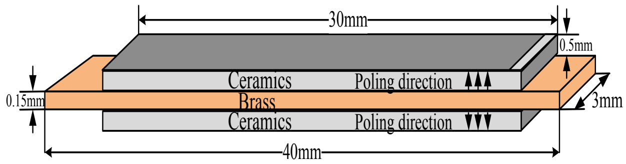

Fig. 1. Specification of bimorph-type piezoelectric actuator.

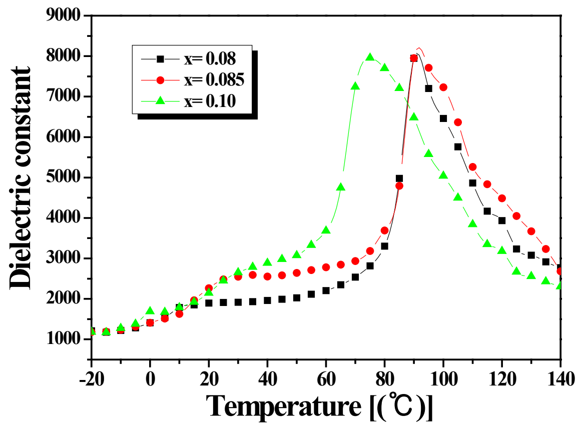

Fig. 2. Temperature dependence of dielectric constant for $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics.

3. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the dielectric constant of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics measured at 1 kHz. Two-phase transitions of orthorhombic-tetragonal (T_{o-t}) and tetragonal-cubic (T_c) phases have been observed. The primary phase transition temperature (T_{o-t}) was identified at near room temperature, and the Curie temperature (T_c) can be found in the range of 75~90℃.

Figure 3 (a) shows the X-ray diffraction (XRD) pattern of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics. A pure perovskite phase was observed for the specimens, and no secondary phase was detected in the XRD measurement range. It is considered that at room temperature the orthorhombic phase and tetragonal phase coexist in $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics. Figure 3(b) shows the expanded X-ray diffraction pattern of the ceramics at the range of 2 θ from 44°to 47°.

Figure 4 shows the SEM micrographs of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics. The average grain size was exhibited as approximately 21 μm for the 0.085 mol Zr substitution ceramics. The addition of CuO with a low melting point effects an improvement in the sinterability, thereby causing the increase of grain size because of the formation of a liquid phase. Also, Cu^{2+} ions can easily cause particle diffusion since they create oxygen vacancies that enter at B-site in the ABO_3 perovskite structure.

Figure 5 shows the temperature dependence of the electromechanical coupling factor (k_p) of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics. The temperature dependence of k_p was measured at an interval of 10℃ in the temperature range of -20℃ to 80℃. The temperature stability of k_p shows relatively good results, and the values were greater than 0.45.

Figure 6 shows the temperature dependence of variations of $\Delta k_p/k_p$20℃ and $\Delta f_r/f_r$20℃ in the temperature range of -20℃ to 80℃ for $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics. $\Delta k_p/k_p$20℃ indicated the maximum value of -0.255 at -20℃. In addition, with increasing temperature, k_p also showed a tendency to increase. It was considered that because of the primary phase transition, the

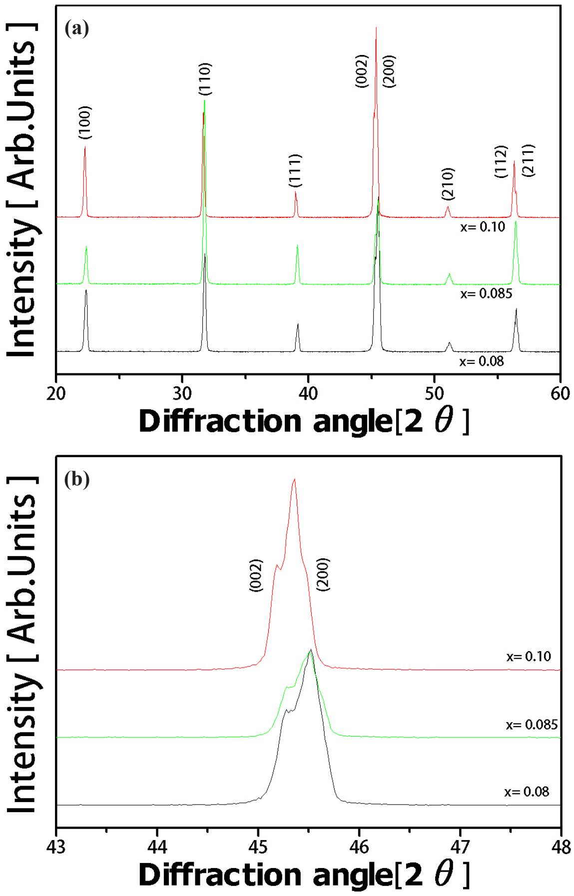

Fig. 3. Temperature dependence of X-ray diffraction pattern of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics in 2 θ range of (a) 20° to 60° and (b) 44° to 47°.

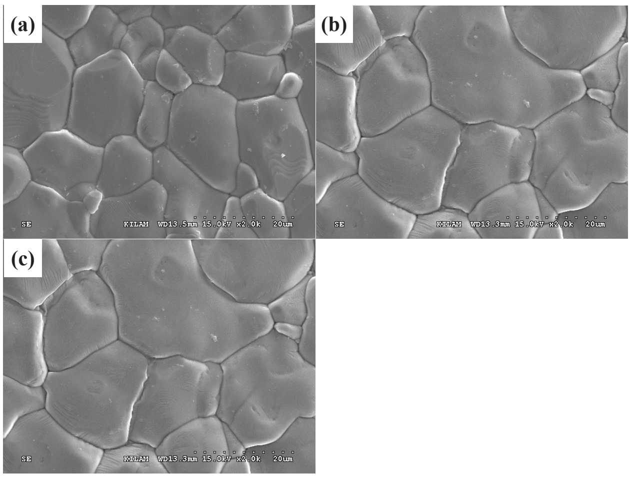

Fig. 4. Scanning electron microscopy (SEM) of the $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics.

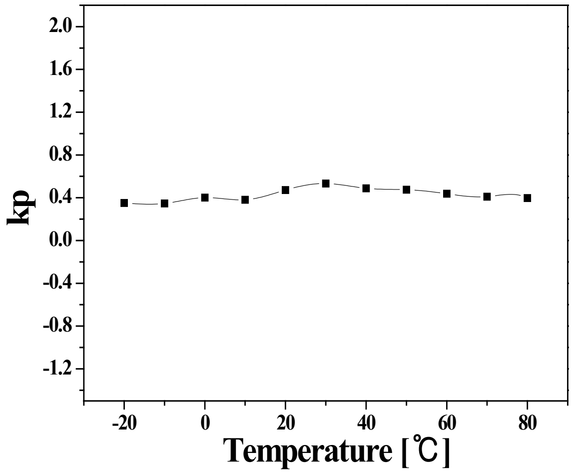

Fig. 5. Temperature dependence of electromechanical coupling factor (k_p) in the temperature range of -20 to 80℃.

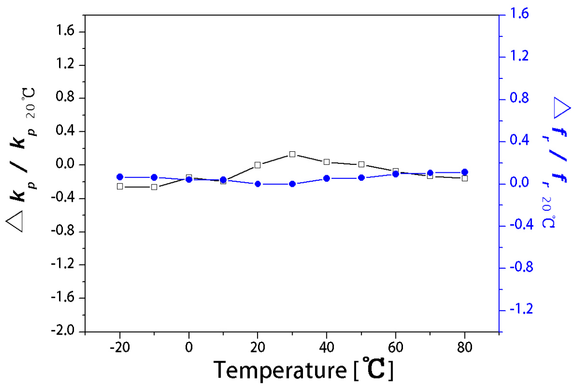

Fig. 6. Temperature dependence of $\Delta k_p/k_p$20℃ and $\Delta f_r/f_r$20℃ in the temperature range of -20 to 80℃.

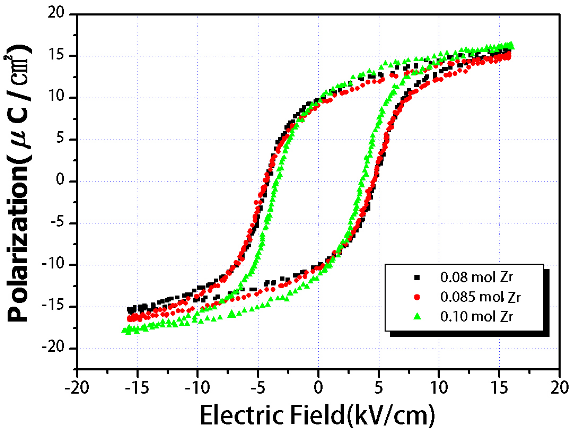

Fig. 7. P-E hysteresis curve of the $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics.

high k_p value was at near room temperature. In addition, the $\Delta f_r/f_r$20℃ exhibited the maximum value of 0.111 at 80℃ and then decreased with increasing temperature of more than 80℃.

Figure 7 shows the P-E hysteresis loop of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics as a function of the temperature. The remnant polarization (P_r) and coercive field (E_c) were 7.5 μC/cm^2 and 3.6 kV/cm, respectively, with the 0.085 mol Zr substitution at room temperature.

Figure 8 shows the total-displacement of the bimorph-type piezoelectric actuator at an optimum frequency of 270 Hz and voltage of 50 V. The total-displacement of the actuator showed a maximum value of approximately 60 μm at 270 Hz and input voltage of 50 V. As a result, according to the optimal driving frequency and voltage, it is considered that the fabricated

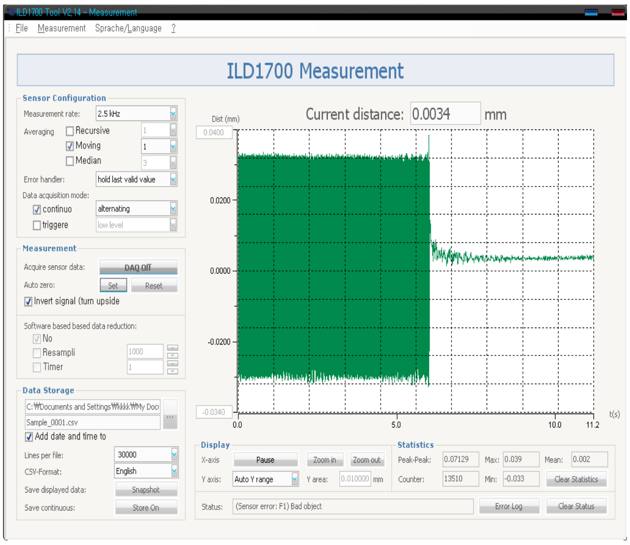

Fig. 8. Total-displacement of bimorph-type piezoelectric actuator at 50 V and 270 Hz.

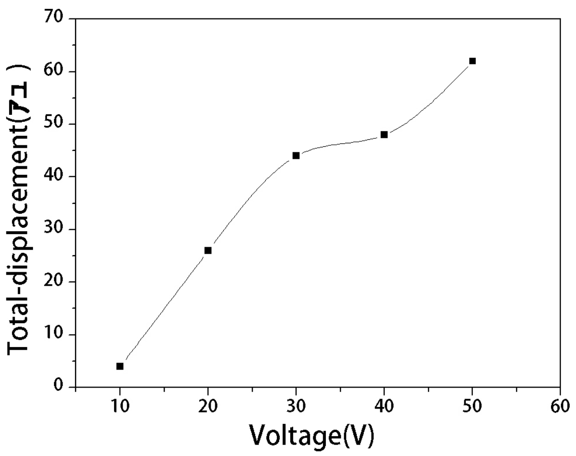

Fig. 9. Total-displacement of bimorph-type piezoelectric as a function of varied voltage at 270 Hz.

bimorph-type piezoelectric actuator can be applied for haptic actuator application. Figure 9 shows the total- displacement of the bimorph-type actuator cam be used as practical application device.

Table 1 shows the physical characteristics of the bimorph-type piezoelectric actuator produced by BCTZ ceramics. The values of the optimal physical characteristics are as follows : piezoelectric coefficient of d_{33} =454 pC/N, electromechanical coupling factor k_p =0.51, dielectric constant ε_r =3,657, mechanical quality factor Q_m =239, and T_c(Tetragonal-Cubic) =90℃, for the 0.085 mol Zr substitution ceramics. It is considered that these physical properties are suitable for lead-free piezoelectric actuator application.

4. CONCLUSION

In this study, $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ lead-free piezo-electric ceramics were synthesized using the conventional solid state reaction method and their dielectric and piezoelectric properties were investigated. In addition, the bimorph-type actuator using $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics was manufactured at the 0.085 mol Zr substitution, and the total-displacement of the actuator was then investigated in detail.

Table 1. Physical properties of the $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics.

x	Density [g/cm^3]	k_p	Dielectric constant	d_{33} [p C/N]	Q_m	T_c
0.08	5.55	0.50	3,435	405	247	90
0.085	5.51	0.51	3,657	454	239	90
0.10	5.56	0.54	3,247	498	234	75

The results are as follows:

1. The X-ray diffraction (XRD) pattern of $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics exhibited a pure perovskite phase, and no secondary phase was detected in the measurement range. $(Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O_3$ ceramics exhibited the optimum piezo electric properties at the 0.085 mol Zr substitution: piezo electric coefficient of d_{33}= 454 pC/N, electromechanical coupling factor k_p= 0.51, dielectric constant ε_r =3,657, mechanical quality factor Q_m= 239, and T_c(Tetragonal-Cubic)= 90℃.

2. $\Delta k_p/k_p$20℃ indicated the maximum value of -0.255 at -20℃. In addition, $\Delta f_r/f_r$20℃ exhibited the maximum value of 0.111 at 80.

3. The total-displacement of the actuator showed the maximum value of approximately 60 μm at 270 Hz and 50 V.

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