Piezoelectric characteristics of inorganic (Na, K, Li) (Nb, Sb, Ta)O₃ – (Bi, Na)(Sr)ZrO₃ ceramics with sintering time

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Abstract. In recent days, the Rhombohedral-Tetragonal (R-T) region composition (Na,K)NbO₃ ceramics have been actively studied because of their excellent piezoelectric properties. In this study, in order to develop the ceramics capable of being sintered at low temperature for piezoelectric actuator, 0.97(Na₀.₁₂₅K₀.₄₅Li₀.₄₇₃)(Nb₀.₆₂₄Sb₀.₃₄Ta₀.₀ ᵃ₃₃)O₃ – 0.03(Bi₀.₃₁Na₀.₃₅Sr₀.₃₆Ta₀.₃₅,ZrO₃) R-T region ceramics were manufactured using the sintering aids of Bi₂O₃–CuO–Fe₂O₃ according to sintering time by the conventional solid state method and their piezoelectric and dielectric properties were systematically investigated. At the 9 hour sintering specimens, the excellent physical properties of d₃₃=244pC/N εr=1475, kₚ=0.44, and Qm=240 were obtained for piezoelectric actuator application.

1. Introduction
Recently, Pb (Zr,Ti)O₃ (PZT) materials were utilized in various kind of devices such as piezoelectric speakers, AE sensors for detecting the rear and side of automobiles, and ultrasonic motor owing to their best piezoelectric and dielectric characteristics [1-2]. But, PbO is composed of more than 60% of the PZT ceramic compositions. Generally, when the ceramics is sintered at above 1200 ° C, the PbO causes environmental pollution and is fatal to peoples because it rapidly volatilizes from the temperature of 1000°C [3-8]. Accordingly, in order to replace Pb–based ceramics, it is required to develop the environmentally friendly ceramics that is comparable to the excellent characteristics of PZT [9].

(Na, K) NbO₃ (NKN) based ceramics reported by Satio et al.in 2004 have excellent piezoelectric properties d₃₃ = 416 [pC / N] and high Tc (Tc = 460 °C). Therefore, the ceramics have been attracting attention as a substitute for PZT system ceramics. However, it is very difficult to manufacture excellent ceramics owing to the volatilization and high deliquescence of alkaline elements of K and Na during sintering at high temperatures [10]. Accordingly, by adding Fe₂O₃, Bi₂O₃, CuO, etc. with low melting point, the liquid phase sintering of the ceramics can be performed at low temperature through prohibiting the volatilization of K and Na, thereby promoting its densification.

In recent years, piezoelectric speakers have been adopted in LG smartphones in korea, which employ laminated piezoelectric actuators that require low-temperature sintering to use the costly Ag-Pd internal electrodes. And also, the d₃₃ and the kp should be large on order to enhance the strain and the characteristics of the piezoelectric actuators, respectively. The excellent physical characteristics of the Pb (Zr,Ti)O₃ system ceramics show in the tetragonal-rhombohedral (R-T) regions [11]. So, the R-T regions of the ceramics have been utilized for manufacturing the piezoelectric devices by many researchers.
Accordingly, in this study, (Na,K,Li)(Nb,Sh,Ta)O$_3$ – (Bi,Na)(Sr)ZrO$_3$ R-T region ceramics were fabricated and their piezoelectric characteristics were investigated.

2. Experimental procedure
In this experiment, the specimens were prepared using a conventional mixed oxide process. The following composition formulas were used:

$$(\text{Na}, \text{K}, \text{Li})(\text{Nb}, \text{Sb}, \text{Ta})\text{O}_3 - (\text{Bi}, \text{Na})(\text{Sr})\text{ZrO}_3 + 0.5\text{wt}\% \text{Bi}_2\text{O}_3 + 0.4\text{wt}\% \text{Fe}_2\text{O}_3 + 0.3\text{wt}\% \text{CuO}$$

The pure reagents of Na$_2$CO$_3$, K$_2$CO$_3$, Sb$_2$O$_5$, Nb$_2$O$_5$, Li$_2$CO$_3$, Ta$_2$O$_5$, Bi$_2$O$_3$, Sr$_2$CO$_3$, ZrO$_2$, Fe$_2$O$_3$, and CuO with more than 99.0% were weighed to $10^{-4}$ g, and the dispersion medium was mixed with acetone in a 3Φ zirconia ball for 24 hours. After drying, they were calcined at 850 °C for 5 hours. The additive Bi$_2$O$_3$, CuO and Fe$_2$O$_3$ were added to the calcined powder, followed by secondary mixing and drying.

A polyvinyl alcohol (5%PVA) was added to the dried powders and the powders were molded under a pressure of 15 MPa with a mold having a diameter of 17Φ. The molded powders were sintered at 1020 °C for 5, 7, 9, and 11 hours. The sintered specimen was polished to a thickness of 1 mm, and the Ag electrode was coated by a screen printing method and then heat-treated at 600 °C for 10 min. A 3 kV / mm electric field was applied to the specimen in a silicon oil bath at room temperature for polarization for 30 minutes. $\varepsilon_r$ and $\tan\delta$ of the polarized specimens were measured using an impedance analyzer (Agilent 4294), and also the its dielectric properties were measured at a frequency of 1 kHz using an LCR meter (Instek LCR-819). Characteristics of the specimens were calculated using the resonance and antiresonance method according to the IEEE standard.

3. Results and discussion
Figure 1 shows the density of specimens with sintering time. The maximum value of the density was 4.403 [g / cm$^3$] in the specimen sintered for 9 hours. These results show that Bi$_2$O$_3$ (817 °C), CuO (1060 °C) and Fe$_2$O$_3$ (730 °C), which have low melting point, added as sintering aids form a liquid phase during the sintering process. It was thought that the formed liquid phase induced the densification of the ceramics. And also, the formed liquid phase was volatilized by over sintering for 11 hours and the density decreased.

Figure 2 shows the piezoelectric constant ($d_{33}$) with sintering time. As the sintering time increased up to 9 hours, the piezoelectric constant increased and then decreased. The maximum value of 244 [pC / N] was obtained for the 9 hours sintered specimen. These results show that as the sintering time increases, the particles grow in the specimen.

![Figure 1. Density of specimens with sintering time.](image-url)
It is considered that the piezoelectric constant ($d_{33}$) is increased because the domain switching of the ceramics is facilitated and the polarization efficiency is increased. The $d_{33}$ value showed the same tendency as that of density.

Figure 2. Piezoelectric constant ($d_{33}$) of specimens with sintering time.

Figure 3 shows the $k_p$ with sintering time. Like the piezoelectric constant, the $k_p$ tends to increase and decrease with increasing sintering time. The maximum value of 0.44 was obtained from the 9 hour sintered specimen. The results can be illustrated by the liquid phase sintering effect of the ceramic particles.
Figure 4. Mechanical quality factor ($Q_m$) of specimens with sintering time.

Figure 4 shows the $Q_m$ with sintering time. As the sintering time increases, the $Q_m$ tends to decrease. These results suggest that the increase of the sintering time induces the increase of the piezoelectric constant $d_{33}$ and the electromechanical coupling factor ($k_p$). As the results, the soft properties of the ceramics enhance, and then the $Q_m$ is decreased.

Figure 5 shows the $\varepsilon_r$ with sintering time. The maximum value of 1475 was obtained for the 9 hour sintered specimen. As the sintering time increased, the dielectric constant also tended to increase because the soft material properties were promoted. Table 1 shows the physical properties of specimens as a function of sintering time.

Figure 5. Dielectric constant ($\varepsilon_r$) of specimens with sintering time.
Table 1. Physical properties of specimens as a function of sintering time.

| Sintering Time (°C) | Density [g/cm³] | k_p | Dielectric constant | d_{33} [pC/N] | Q_m |
|---------------------|-----------------|-----|---------------------|---------------|-----|
| 5                   | 4.392           | 0.415 | 1414               | 231           | 294 |
| 7                   | 4.395           | 0.427 | 1442               | 221           | 272 |
| 9                   | 4.403           | 0.440 | 1475               | 244           | 240 |
| 11                  | 4.374           | 0.431 | 1495               | 237           | 235 |

4. Conclusions
In this study, (Na,K,Li)(Nb,Sb, Ta)O_3 – (Bi,Na, (Sr) ZrO_3 R-T region ceramics were manufactured using the sintering aids of Bi_2O_3-CuO-Fe_2O_3 according to sintering time and their piezoelectric characteristics were systematically investigated.

1. The maximum value of the density was 4.403 [g/cm³] in the specimen sintered for 9 hours
2. At 9 hours sintered specimens, the excellent physical properties of d_{33}=244pC/N ε_r=1475, k_p=0.44, and Q_m=240 were obtained for piezoelectric actuator application.

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