Piezoelectric characteristics of inorganic 0.965(Na, K, Li)(Nb, Sb)O₃–0.035(Bi, Na)(Sr)ZrO₃ ceramics doped with Fe₂O₃ for actuator

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Abstract. In this experiment, 0.965(Na,K,Li)(Nb,Sb)O₃–0.035(Bi,Na)(Sr)ZrO₃ ceramics were fabricated with Fe₂O₃ addition, and their piezoelectric characteristics were investigated. When Fe₂O₃ was added to the ceramics, d₃₃ and kₚ were decreased. However, Qm was increased. At the NKN-BNZ ceramics with 0.1 wt% Fe₂O₃, the d₃₃, kₚ, Qm, and εₑ were optimized as 263[pC/N], 0.450, 51.94, 1978, respectively.

1. Introduction

In recent years, Lead Zirconate Titanate (PZT) system piezoelectric ceramics have been used extensively in ultrasonic dishwashers, smartphone piezoelectric speakers, and ultrasonic surgical instruments [1]. However, they contain at least 60 wt% PbO in the composition in spite of having excellent piezoelectric properties. PbO is regulated as environmentally harmful substance because it volatilizes rapidly at 1000°C and is harmful to human body [2-3].

(Na,K)NbO₃-based piezoelectric ceramics with d₃₃ = 416[pC/ N] developed by Sato et al. in 2004 have been actively studied as a substitute material for PZT system because of their excellent piezoelectric properties. However, it is hard to manufacture the dense ceramics due to volatilization of potassium and sodium at high temperature in the NKN system.

In addition, the piezoelectric properties of NKN system ceramics are very high in the orthorhombic–tetragonal phase boundary regions, and it is difficult to actually apply to the application device because the piezoelectricity changes greatly at this orthorhombic–tetragonal transition (To-t) temperature.

In recent years, Jianguo Zhu et al. have developed a composition with best d₃₃ of ~350 (pC/N) and high Tc of ~315 (°C) in the NKN ceramics substituted with (Bi₀.₅ Na₀.₅)ZrO₃ having a rhombohedral-tetragonal(RT) phase boundary regions [4].

Here, (Bi₀.₅ Na₀.₅) ZrO₃ can shift T_R-O (rhombohedral-tetragonal transition point) and T_O-T (orthorhombic-tetragonal transition point) of (Na, K) NbO₃ ceramics to room temperature. As the result, by forming the R and T phases coexistence, high d₃₃ and high Tc can be obtained. Originally, PZT composition ceramics with a rhombohedral-tetragonal (RT) phase regions has been extensively used because of its excellent piezoelectric properties [5]. Nowadays, smartphone piezoelectric speakers have been mounted in LG G8 phone. A high kp and high d₃₃ are required for this device.
Accordingly, in this experiment, for developing NKN composition ceramics with a rhombohedral-tetragonal (RT) phase regions, (Na,K)NbO$_3$ system substituted with (Bi,Na)(Sr) ZrO$_3$ were fabricated as a function of Fe$_2$O$_3$ addition and their piezoelectric characteristics were analyzed for piezoelectric speakers.

2. Experiments
We manufactured the ceramic specimens as following composition formula:

$$0.965\, (\text{Na,K,Li})(\text{Nb,Sb})\text{O}_3 - 0.035\, (\text{Bi,Na})(\text{Sr})\text{ZrO}_3 + x\, \text{wt}\% \text{Fe}_2\text{O}_3 (x=0, 0.1, 0.2, 0.3, 0.4)$$

The high purity powders of K$_2$CO$_3$, Na$_2$CO$_3$, Li$_2$CO$_3$, Sb$_2$O$_5$, SrCO$_3$, Bi$_2$O$_3$, and ZrO$_2$ with the purity of above 99% were weighed by mole ratio and the high purity powders were milled for 24 hours. And then, they were calcined at 900°C for 6 hours. And then a 5 wt % polyvinyl alcohol was mixed to the powders. The pressure of 17 MPa using a mold with diameter of 9 mm were induced, and then sintered at 1130°C for 3h. The samples were polished to thickness 1.0mm and then electro-deposited with Ag paste. Capacitance was measured at 1 kHz using an LCR meter (ANDO AG-4034) and the dielectric constant (ε$_r$) was calculated for investigation of the dielectric characteristics. For analysis of the piezoelectric characteristics the fr and fa were measured by an Agilent 4294A Impedance Analyzer and then the k$_p$ and Q$_m$ were calculated. d$_{33}$ was measured by APC-90-2030 piezo d$_{33}$ meter.

3. Results and discussion
The density of the specimen with x(=Fe$_2$O$_3$) was appeared in Figure 1. The density enhanced due to the increase of the Fe$_2$O$_3$. In this experiment, Fe$_2$O$_3$ (melting point: 730°C) and Bi$_2$O$_3$ (melting point: 817°C) were added for forming the liquid phase of the samples during firing period.

![Figure 1. Density of samples with Fe$_2$O$_3$ addition.](image-url)

However, these oxides firstly added before calcination process. Accordingly, except for acting as liquid phase, Fe$_2$O$_3$ can be acted as acceptor dopant. The result of the density is because the densification of the samples was increased up to 0.1 wt% as liquid phase effect and then slowly decreased owing to excess Fe$_2$O$_3$.
Figure 2 shows the kp of the specimen with Fe$_2$O$_3$ addition. A maximum value of 0.450 was obtained when the Fe$_2$O$_3$ was 0.1 because of the enhancement of sinterability. Thereafter, the kp was decreased. And then, the kp increased again when the Fe$_2$O$_3$ was 0.3. The decrease of kp at the 0.2 wt% Fe$_2$O$_3$ composition is considered because Fe$_2$O$_3$ was largely acted as acceptor dopant.

![Figure 2. Kp of samples with Fe$_2$O$_3$](image)

The Qm with Fe$_2$O$_3$ is shown in Figure 3. When Fe$_2$O$_3$ substitution is 0.2, the highest value of 55 was appeared, and then decreased a little. This result is because Fe$^{3+}$ ion (0.64 Å) can be infiltrated at the B sites of Nb$^{5+}$ ion (0.69 Å) and Sb$^{5+}$ ion (0.62 Å). As the result, the formation of oxygen vacancies are caused, resulting in the increase of Qm through restraining the domain wall motion.

![Figure 3. Qm of samples as a function of Fe$_2$O$_3$](image)
The $d_{33}$ piezoelectric constant with $\text{Fe}_2\text{O}_3$ is shown in Figure 4.

The best value of $d_{33}$ was $263$ [pC / N] when $\text{Fe}_2\text{O}_3 = 0.1$. In this composition, perhaps, it is considered that rhombohedral and tetragonal (R-T) coexistence phases were appeared. And also, the decrease of $d_{33}$ at the 0.2 wt% $\text{Fe}_2\text{O}_3$ composition is considered because $\text{Fe}_2\text{O}_3$ was largely acted as acceptor dopant. In general, in case of acting as acceptor dopant, $Qm$ increases and $k_p$ and $d_{33}$ decreases through restraining the domain wall motion.

Figure 4. $d_{33}$ of samples with $\text{Fe}_2\text{O}_3$.

Figure 5. $\varepsilon_r$ (dielectric constant) of samples with $\text{Fe}_2\text{O}_3$. 
The $\varepsilon_r$ (dielectric constant) according to Fe$_2$O$_3$ is shown Figure 5. The best value of $\varepsilon_r$ was 2014 [pC/N] at the Fe$_2$O$_3$= 0. After x of Fe$_2$O$_3$ was more than 0.1, $\varepsilon_r$ was abruptly decreased because Fe$_2$O$_3$ also acts as acceptor dopant. Table 1 shows electrical characteristics of samples with Fe$_2$O$_3$.

| X  | Density [g/cm$^3$] | $k_p$ | d$^{33}$ [pC/N] | $Q_m$ |
|----|-------------------|------|----------------|------|
| 0  | 4.515             | 0.436| 2014           | 53.04|
| 0.1| 4.542             | 0.450| 1978           | 51.74|
| 0.2| 4.539             | 0.406| 1968           | 55   |
| 0.3| 4.537             | 0.444| 1944           | 53.44|
| 0.4| 4.491             | 0.436| 1833           | 53.83|

4. Conclusions
In this experiment, 0.965(Na,K,Li)(Nb,Sb)O$_3$−0.035(Bi ,Na)(Sr)ZrO$_3$ ceramics were fabricated with Fe$_2$O$_3$, and their piezoelectric characteristics were investigated.

- The $d_33$ and $k_p$ were decreased when Fe$_2$O$_3$ was added to the ceramics. But $Q_m$ was increased.
- At the NKN-BNZ ceramics with 0.1 wt% Fe$_2$O$_3$, the $d_33$, $k_p$, $Q_m$, and $\varepsilon_r$ were optimized as 263[pC/N], 0.450, 51.94, 1978, respectively, for piezo-actuators.

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