Dielectric and piezoelectric properties of (0.10-x) Pb (Mn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} -x Pb(Ni\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-0.91Pb(Zr\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3} ceramics with high $Q_m$

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Abstract. In this paper, for developing the piezoelectric ceramics suitable for ultrasonic surgical instruments application, (0.10-x) Pb(Mn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} -x Pb(Ni\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}- 0.91 Pb(Zr\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3} (x=0. 0.015, 0.03, 0.045, 0.06, 0.075) ceramics were manufactured and then their physical characteristics were systematically analyzed. When Pb(Ni\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} and sintered temperature were is 0 mol\%, 940°C, respectively their piezoelectric characteristics $Q_m$= 1982, $Q_m$= 1982 were obtained for ultrasonic surgical instruments and actuators.

1. Introduction

Recently, Pb(Zr,Ti)O\textsubscript{3} (PZT) system ceramics has been actively studied for the application of piezoelectric ceramics such as ultrasonic sensor, ultrasonic cleaners, ultrasonic surgical instruments and piezoelectric actuators [1]. Although Pb(Zr,Ti)O\textsubscript{3} ceramics have been widely utilized in the various kind of fields, deterioration of piezoelectric characteristics and environmental pollution due to PbO, which is rapidly volatilized at around 1000°C, are problematic.

Therefore, for solving the PbO problems, the studies on the two, three component system PZT, and PMN-PZT ceramics have been actively performed in order to further more increase physical properties together with lowering the sintering temperature of the ceramics. Therefore, to decrease the sintering temperature and to increase the piezoelectric characteristics is to use various kinds of additives as sintering aids [2,3]. Recently, ultrasonic surgical instruments for laparoscopic surgery have been widely used. The ultrasonic surgical instrument uses a piezoelectric vibrator, which generates heat due to high-power driving for a long time. The generated heat promotes thermal expansion of the piezoelectric vibrator and can cause destruction.

Therefore, it is necessary to effectively design the ultrasonic surgical instrument for radiating the heat generated well even if it is used for a long time. And also, it is required to increase $Q_m$ for reducing the heat rise of the piezoelectric vibrator.

The piezoelectric ceramic materials with high $Q_m$ for ultrasonic surgical instrument application may be achieved by developing Pb(Ni\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}- Pb(Zr\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}- Pb(Mn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} system. Moreover, in the system ceramics, dielectric and piezoelectric properties can be greatly enhanced by the variations of composition. The additives of Li$_2$CO$_3$, CuO, Bi$_2$O$_3$ can induce liquid phase state of the system, causing the enhancement of the physical properties [4-7].

Here, in order to develop the system ceramics with high kp and high Qm for ultrasonic surgical instruments and actuators applications,
CuO, Bi$_2$O$_3$ and Li$_2$CO$_3$ (CLBO) as additives were used to (0.10-x) Pb(Mn$_{0.3}$Nb$_{0.7}$)O$_3$-x Pb(Ni$_{0.2}$Nb$_{0.8}$)O$_3$-0.91 Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (x=0. 0.015, 0.03, 0.045, 0.06, 0.075) ceramics. Here, x was varied for investigating the physical characteristics of the manufactured ceramics.

2. Experiments
In this study, the used compositions are as follows:

\[(0.10-x) \text{Pb(Mn}_{0.3}\text{Nb}_{0.7}\text{)O}_3 \text{-x Pb(Ni}_{0.2}\text{Nb}_{0.8}\text{)O}_3 \text{-0.91 Pb(Zr}_{0.2}\text{Ti}_{0.8}\text{)O}_3 +0.5\text{wt}\% \text{ PbO (x=0. 0.015, 0.03, 0.045, 0.06, 0.075)} + \text{additives (Li}_2\text{CO}_3 \text{- CuO} \text{-Bi}_2\text{O}_3)\]

The PbO, MnO$_2$, ZrO$_2$, TiO$_2$, NiO and Nb$_2$O$_5$ materials with purity more than 99% were weighed and then were ball-milled for 24 hours. And then they were also calcined at 850°C for 2 hours. And then, Li$_2$CO$_3$- CuO-Bi$_2$O$_3$ as additives was added and ball-milled again for 24 hours. 5 wt% PVA was added and mixed to the calcined ceramic powders. The ceramic powders were molded under a pressure of 15 MPa. And then the molded powders were sintered at 940°C for 2 hours. For investigating the physical properties, the ceramic specimens were polished to thickness 1 mm. And then were electrodeposited with silver paste. The poling of specimens was made by 30 kV/cm for 30 minutes in 120°C silicon oil bath. The capacitance was measured by an LCR meter (Instek LCR-819) and the dielectric constant (\(\varepsilon_r\)) was measured. At the room temperature, the resonant frequency \(f_r\) and anti-resonant frequency \(f_a\) were investigated by Agilent 4294A Impedance Analyzer. And then the \(Q_m\) and \(k_p\) were measured. Piezoelectric \(d_{33}\) constant was measured by \(d_{33}\) meter (APC-90-2030).

3. Results and discussion
Figure 1 shows the density of the specimen with x (=Pb(Ni$_{0.2}$Nb$_{0.8}$)O$_3$). The density showed the highest value of 8.24 g/cm$^3$ at the 3 mol% x. It is analyzed that Bi$_2$O$_3$, CuO, and Li$_2$CO$_3$ with a low melting temperature can react with PbO for forming liquid phase, resulting in the increase of densification.

Figure 2 shows the \(k_p\) of the specimen with x. The \(k_p\) showed the highest value of 0.62 at 6 mol% x, and then gradually decreased. In general, the \(k_p\) is enhanced when the sintered density of the ceramics is increased. However, density was decreased due to excess PNN substitution but \(k_p\) showed the trend of increment according to the movement toward MPB composition [8]. Figure 3 shows the piezoelectric \(d_{33}\) constant of the specimen with x. When x was 7.5 mol%, the \(d_{33}\) maximum value was 350 pC/N, and then the piezoelectric \(d_{33}\) constant decreased.

Figure 1. Density of the specimen with x.
Figure 2. $K_p$ of the specimen with $x$.

Figure 3. $d_{33}$ of the specimen with $x$.

In this study, it can be explained by the fact that the $d_{33}$ values were slightly increased due to the increase of $x$ with -120°C Curie temperature.

Figure 4 shows the dielectric constant of the specimen with $x$ carried out at room temperature. The dielectric constant showed the highest value of 1,345 at 7.5 mol% $x$. This is a similar result with $d_{33}$.

This result can be also illustrated by the fact that Curie temperature of the specimen is decreased according to the increase of PNN with -120°C Curie temperature. Accordingly, the dielectric constant of the specimen at room temperature is increased.

Figure 5 shows the $Q_m$ with $x$.

According to $x$ substitution, the content of MnO$_2$ which coexist in the Mn$^{3+}$ state in PZT systems as the substitutes for Zr$^{4+}$ and Ti$^{4+}$ can be decreased. Thus, the generated oxygen vacancies is decreased, causing a decrease in the $Q_m$. At the 0 mol% $x$, the highest value of $Q_m$ was 1982.

These phenomenon can be illustrated by the fact that the decrease of Mn ratio increases the ratio of $x$. As the results, As the Mn ratio was small, the $Q_m$ was decreased.
4. Conclusions
In order to develop low temperature sintering piezoelectric ceramics for ultrasonic surgical
instruments and actuators, $(0.10-x)$ Pb(Mn$_{0.3}$Nb$_{0.7}$)O$_3$-$x$ Pb(Ni$_{0.3}$Nb$_{0.7}$)O$_3$-$0.91$ Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ +0.5 wt% PbO were fabricated with the variation of Pb(Ni$_{0.3}$Nb$_{0.7}$)O$_3$. The piezoelectric and dielectric properties of the manufactured samples were investigated. The following results were obtained:

- At the 3 mol% Pb(Ni$_{0.3}$Nb$_{0.7}$)O$_3$, the maximum density of 8.25 g/cm$^3$ was obtained.
- At 0 mol% Pb(Ni$_{0.3}$Nb$_{0.7}$)O$_3$ composition, physical characteristics of $d_{33} = 236$ pC/N, $\varepsilon_r = 732, k_p = 0.5839, Q_m = 1982$ were obtained, suitable for ultrasonic surgical instruments.

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