Effect of CuO on the Low Temperature Sintering Properties of PSN-PNN-PZT Ceramics

Yeong-Ho Jeong
Korea Electric Power Research Institute, Yusung-Gu, Taejon 305-380, Korea

Ju-Hyun Yoo[a] and Seung-Hyon Nam
Department of Electrical Engineering, Semyung University, Jechon, Chungbuk 390-711, Korea

Su-Ho Lee
Department of Electrical Engineering, Kyungsung University, Pusan 390-711, Korea

Kwang-Hyun Chung and Duck-Chool Lee
Department of Electrical Engineering, Inha University, Incheon 402-751, Korea

[a]E-mail : juhyun57@semyung.ac.kr

(Received March 5 2004, Accepted June 1 2004)

In this study, in order to develop the low temperature sintering ceramics for ultrasonic vibrator, $Pb(Sb_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.48}Ti_{0.52})O_3$ ceramics were manufactured as a function of the amount of CuO addition, and their dielectric and piezoelectric characteristics were investigated. With increasing CuO addition, the grain size and density increased up to 0.3 wt% CuO addition. Taking into consideration electromechanical coupling factor(k_p) of 0.53, mechanical quality factor(Q_m) of 423, dielectric constant(ε_r) of 1,759 and piezoelectric constant(d_{33}) of 362pC/N, it could be concluded that 0.5 wt% CuO added composition ceramic sintered at 920 °C was suitable for ultrasonic vibrator application.

Keywords : Low sintering temperature, CuO addition, Ultrasonic vibrator, Piezoelectric constant

1. INTRODUCTION

Recently, the applications of piezoelectric ceramics are remarkably getting expanded to piezoelectric transformer, ultrasonic vibrator, ultrasonic motor, filter and resonator etc[1,2]. Especially, about the piezoelectric ultrasonic vibrator, many researches are gone to improve the piezoelectric properties such as the electro-mechanical coupling factor(k_p), mechanical quality factor(Q_m) and dielectric constant by adding single or complex oxide etc to PZT family and ternary component ceramics that show the superior piezoelectric properties[3,4].

Moreover, because the piezoelectric devices that convert electrical energy to mechanical energy require the high strength mechanical properties, research about the piezoelectric ultrasonic vibrator that shows the superior mechanical properties is being strongly performed. When most PZT family ceramics containing PbO are manufactured, a lot of PbO is rapidly volatilized over 1,000 °C. And also, as it is revealed that the volatilization of PbO is also a major reason of environmental pollution, the concern about the development of the low temperature sintering piezo-electric ceramics, which can be sintered below 1,000 °C, and Pb-free piezoelectric materials are getting larger[5]. In this study, in order to develop the composition ceramics capable of being sintering at low temperature for ultrasonic vibrator application, the complex oxides like $BiFeO_3$ and $Pb(Co_{1/2}W_{1/2})O_3$ which show the effect of low temperature sintering were added to $Pb(Sb_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.48}Ti_{0.52})O_3$ ceramics with high dielectric constant and superior piezoelectric properties. And piezoelectric and dielectric properties were investigated according to CuO addition.

2. EXPERIMENT

The specimens were manufactured using a conventional mixed oxide process. The composition used in this

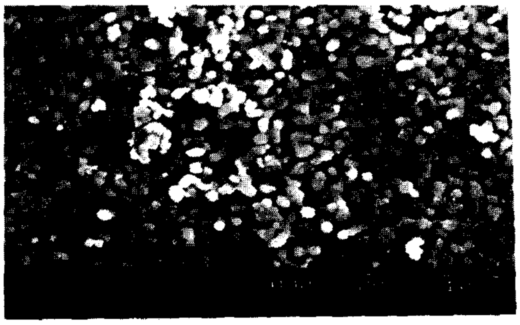
study was as follows;
$0.91Pb[(Sb_{1/2}Nb_{1/2})_{0.02}(Zr_{0.48}Ti_{0.52})_{0.85}(Ni_{1/3}Nb_{2/3})_{0.13}]O_3+$
$0.05BiFeO_3+0.04Pb(Co_{1/2}W_{1/2})O_3+Xwt\%CuO+0.5wt\%$
MnO_2, (X=0, 0.3, 0.5 and 0.7)

First of all, $Pb(Co_{1/2}W_{1/2})O_3$ was weighted by molar ratio and the powders were ball-milled for 24h and pre-synthesized for 2h at 880 °C. The rest powders were added to $Pb(Co_{1/2}W_{1/2})O_3$ powders and the mixtures were ball-milled again for 24h. After drying them, they were calcined at 850 °C for 2h. And, CuO was added to them and they were mixed again. A polyvinyl alcohol (PVA: 5 %) was added to dried powders and it was molded by the pressure of 1,000kg/cm^2 in 21mmΦ mold and then sintered at 885~950 °C for 2h. For measurement of the piezoelectric characteristics, the specimens were polished to 1mm thickness and then electrodeposited with Ag paste. And poling was carried out at 120 °C in a silicon oil bath by applying fields of 30kV/cm for 10 min. All samples were aged for at least 24h prior to measure the piezoelectric and dielectric properties. For investigating the dielectric properties, capacitance was measured at 1kHz by LCR meter(ANDO AG-4034) and dielectric constant was calculated. For investigating the piezoelectric properties, the resonant and anti-resonant frequencies were measured by Impedance Analyzer (Agilent 4294) according to IRE standard and then electromechanical coupling factor and mechanical quality factor were calculated.

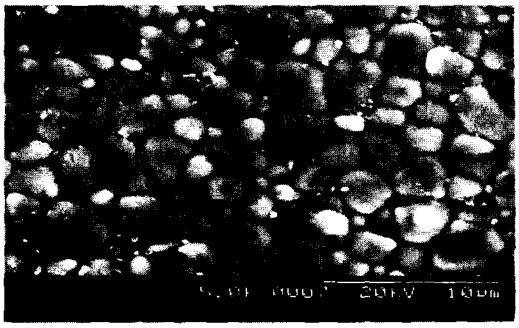
3. RESULTS AND DISCUSSION

Figure 1 shows microstructures of specimens sintered at 920 °C according to the amount of CuO addition. As the increase of CuO addition, grain size increased. The growth of a grain was accelerated by the reason that CuO was reacted with PbO and formed the liquid phase of Cu_2O-PbO[6].

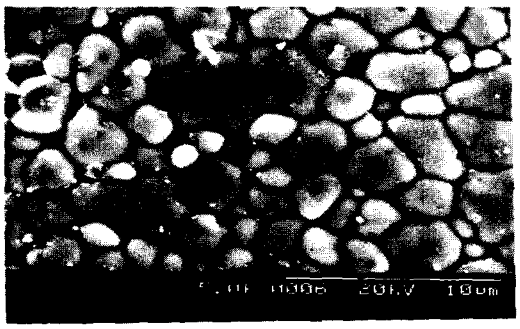
Figure 2 shows the changes of the density according to the various sintering temperatures and CuO contents. According to the increase of CuO addition, the density of specimens increased and showed the maximum value of 7.89 g/cm^3 at 0.3 wt% CuO addition and sintering temperature of 920 °C. But it decreased over 0.5 wt% CuO addition. It can be analyzed by the fact that the density goes down by over-addition of CuO amount. Also, the changes of density over the 0.3 wt% CuO addition showed almost same magnitude at the sintering temperature of 920 °C and 950 °C. Therefore, it could be concluded that the optimum sintering temperature was 920 °C.



(a) CuO 0 wt%



(b) CuO 0.3 wt%



(c) CuO 0.5 wt%

Fig. 1. SEM with the amount of CuO addition(920 ℃).

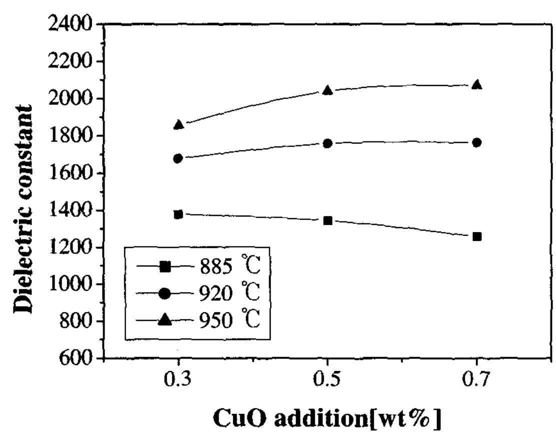


Fig. 2. Density with the amount of CuO addition.

Figure 3 shows electromechanical coupling factors(k_p) according to the variation of the sintering temperature and the amount of CuO addition. The electromechanical coupling factor showed the maximum value of 0.54 at the sintering temperature of 950 °C and 0.3 wt% CuO addition. Figure 4 shows the mechanical quality factors(Q_m) according to the variation of the sintering temperature and the amount of CuO addition. Mechanical quality factor of specimens sintered at 920 °C showed the maximum value of 423 at 0.5 wt% CuO addition, and then it decreased over the 0.5 wt% CuO addition. That of specimens sintered at 885 °C and 950 °C decreased according to the amount of CuO addition.

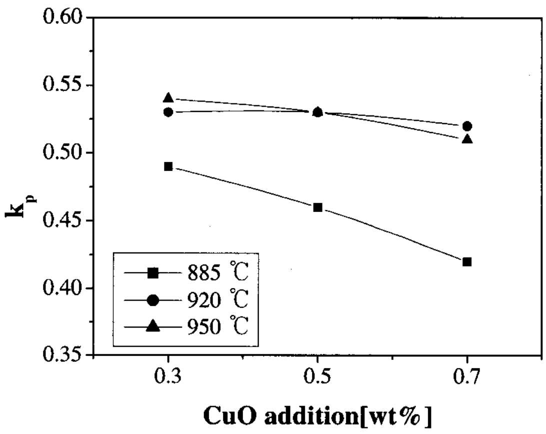


Fig. 3. Electromechanical coupling factor(k_p) with the amount of CuO addition.

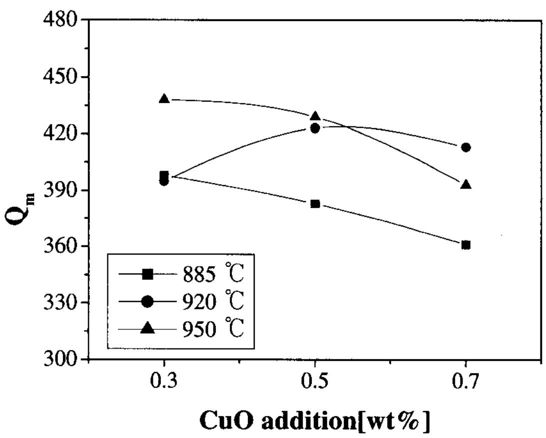


Fig. 4. Mechanical quality factor(Q_m) with the amount of CuO addition.

From these results, the simultaneous increase of k_p and Q_m values according to CuO addition at 920 °C can be illustrated by the facts that CuO addition enhance the densification of specimens at low temperature by forming the liquid phase of $PbO-Cu_2O$ and at the same time CuO reacts as a hardner producing O-vacancy in the PZT composition ceramics, by substituting Cu^{2+}(0.73 Å) for Ti^{4+}(0.68 Å).

Figure 5 shows piezoelectric constant(d_{33}) according to the variation of the sintering temperature and the amount of CuO addition. The characteristics of piezoelectric constant coincided with the properties of k_p, and showed the maximum value of 368pC/N at 0.3 wt% CuO addition and sintering temperature of 950 °C.

Figure 6 shows the dielectric constant according to the variation of the sintering temperature and the amount of CuO addition. As the sintering temperature increased, it had a tendency that the dielectric constants increased. It can be illustrated by the fact that the grain size increases according to the sintering temperature[7].

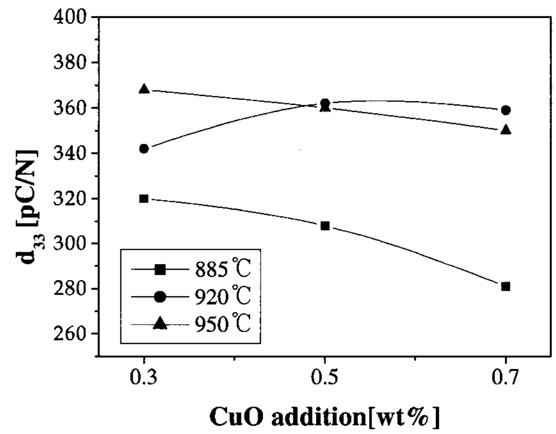


Fig. 5. Piezoelectric constant(d_{33}) with the amount of CuO addition.

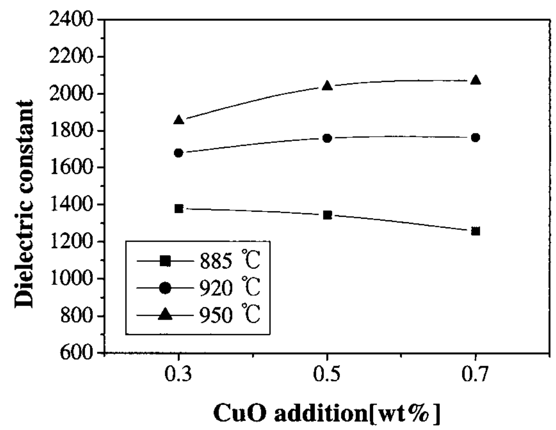


Fig. 6. Dielectric constant(ε_r) with the amount of CuO addition.

The dielectric constant decreased according to the amount of CuO addition at the sintering temperature of 885 °C. However the dielectric constant increased up to 0.5 wt% CuO addition at the sintering temperature of 920 °C and 950 °C, and then got saturated over 0.5 wt% CuO addition. That is, the dielectric constant increased by increase of the density according to the sintering temperature and that of specimens according to the amount of CuO addition at each of sintering temperature was decreased after the maximum value because of segregating the sintering aid with a low dielectric constant to grain boundary by amorphous forms. Consequently, CuO addition in the PZT composition ceramics could derive low temperature sintering, and at the same time improved piezoelectric properties.

4. CONCLUSIONS

In this study, in order to develop the piezoelectric ceramics for ultrasonic vibrator, which has a high dielectric constant, electromechanical coupling factor and mechanical quality factor and is possible for low temperature sintering, $Pb(Sb_{1/2}Nb_{1/2})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.48}Ti_{0.52})O_3$ ceramic's dielectric and piezoelectric characteristics were investigated according to the amount of CuO addition.

1. As the amount of CuO addition increased, the grain size increased, and the density increased up to 0.3 wt% CuO addition, however, got saturated over 0.3 wt% CuO addition.

2. CuO addition enhance the densification of specimens at low temperature by forming the liquid phase of PbO-Cu_2O and at the same time CuO reacts as hardner producing O-vacancy in the PZT composition ceramics, by substituting Cu^{2+}(0.73 Å) for Ti^{4+}(0.68 Å).

3. The density, dielectric constant, electromechanical coupling factor(k_p), mechanical quality factor(Q_m) and piezoelectric constant showed the optimum value of 7.88 g/cm^3, 1759, 0.53, 423 and 362 pC/N, respectively, at 0.5 wt% CuO addition and the sintering temperature of 920 °C for ultrasonic vibrator application.

ACKNOWLEDGMENT

This work has been supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce, Industry and Energy of the Korean Governments.

REFERENCES

[1] Y. W. Lee, J. H. Yoo, K. H. Yoon, H. S. Jeong, S. J. Suh, and J. S. Kim, "Piezoelectric ceramic transformer operating in thickness extensional vibration mode for power supply", J. of KIEEME(in Korean), Vol. 13, No. 4, p. 286, 2000.

[2] O. Ohnishi, H. Kishie, A. Iwamoto, Y. Sasaki, T. Zaitsu, and T. Inoue, "Piezoelectric ceramic transformer operating in thickness extensional vibration mode for power supply", IEEE Ultrasonics Symposium Proc., p. 483, 1992.

[3] B. Jaffe, W. R. Cook, and H. Jaffe, "Piezoelectric Ceramics", Academic Press , London, p. 148, 1971.

[4] Yuhuan Xu, "Ferroelectric Materials and Their Application", Elsevier, Amsterdam, p. 140, 1991.

[5] T. Takenaya, K. Maruyama, and K. Sakata, "$(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ System for lead-free piezoelectric ceramics", Jpn. J. Appl. Phys., Vol. 30, No. 9B, p. 2236, 1991.

[6] E. M. Levin, C. R. Robbins, and H. F. Mcmurdie, "Phase Diagrams for Ceramists", The American Ceramic Society, p. 86, 1979.

[7] C. Tapaonoi, S. Tashiro, and H. Igarashi, "Piezoelectric properties of fine-grained lead zirconate titanate ceramics modified with $Pb(Sb_{1/2}Nb_{1/2})O_3$", Jpn. J. Appl. Phys., Vol. 33, No. 9B, p. 5336, 1994.