Electronic Materials Letters, Vol. 4, No. 4 (2008), pp. 189-192

Effect of CuO Additions on Microstructures and Electromechanical Properties of $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.25PbZrO_3$-$0.35PbTiO_3$ Ceramics

Min-Soo Kim,* Sohyun Jeon, Soon-Jong Jeong, In-Sung Kim, and Jae-Sung Song

Piezoelectric Devices Research Group, Korea Electrotechnology Research Institute, Changwon 641-120, Korea

The effect of CuO additions on the microstructures and electromechanical properties of $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.25PbZrO_3$-$0.35PbTiO_3$ ceramics was investigated. Samples with CuO addition were synthesized by ordinary sintering technique. X-ray diffraction patterns indicated that all samples formed a single phase perovskite structure. The addition of CuO improved the sinterability of the samples and caused an increase in the density and grain size at low temperature. The optimum sintering temperature was lowered by CuO additions. Excellent piezoelectric and electromechanical responses, d_{33}~663 pC/N, k_P~0.72, were obtained for the samples of high density with 0.1 wt% CuO addition sintered at 1050°C for 4 h in air.

Keywords: PMNZT, CuO, piezoelectric, microstructure, sintering

1. INTRODUCTION

Lead oxide based ceramics, represented by PZT, are the most widely used materials for piezoelectric actuators, sensors, and transducers due to their excellent piezoelectric properties.[1-3] In particular, high-performance multilayered piezoelectric ceramics for advanced electronic components have drawn great attention. These piezoelectric devices require cofiring with an internal electrode; Ag-Pd alloy is mainly used.[4,5] The development of low-temperature sintering techniques has been required for the fabrication of electronic ceramics because of energy consumption reduction and reproducibility improvement.[6] Furthermore, the suppression of any reaction between the ceramics and internal electrodes can be expected for the fabrication of multilayer devices. Low-temperature sintering offers the advantage of using noble metal electrodes, such as Ag, Ni or Cu, instead of expensive Ag-Pd alloys, and solves the problem of PbO volatilization causing compositional fluctuation and environmental contamination.[3]

Several low-temperature sintering techniques have been reported for lead-based piezoelectric ceramics such as hot-pressing in oxygen,[7] use of fine powder,[8] additives that enhance solid state sintering[9] and additives with low melting points in the synthesized materials.[10-16] The most popular of these techniques is the addition of oxides or compounds, which have low melting temperatures and assist in sintering. Many additives have been tested for low temperature sintering of PZT, including $BiFeO_3$-$Ba(Cu_{0.5}W_{0.5})O_3$,[10] Li_2CO_3-Bi_2O_3-$CdCO_3$,[11] MnO_2-CuO-Al_2O_3,[12] $LiBiO_2$,[13] 4PbO-B_2O_3,[14] and B_2O_3-Bi_2O_3-CdO[15] and NaF-V_2O_5-PbO-CuO.[16]

In this study, the synthesis process was confined to the conventional sintering process. In order to develop piezoelectric ceramics capable of being sintered at low temperature for multilayer piezoelectric device applications, $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.25PbZrO_3$-$0.35PbTiO_3$ (PMNZT) composition ceramics with high electromechanical properties were selected[17] and CuO additions were used as sintering aids. The effect of CuO additions on the microstructures and piezoelectric properties of the PMNZT ceramics was investigated.

2. EXPERIMENTAL PROCEDURE

Reagent-grade oxide powders of PbO, ZrO_2, TiO_2, MgO, Nb_2O_5 and CuO were used as raw materials. Samples with a composition of $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.25PbZrO_3$-$0.35PbTiO_3$ (PMNZT) were synthesized using the columbite precursor method.[18] The powders were mixed by ball milling in ethanol for 24 h with stabilized ZrO_2 media. PbO, ZrO_2 and TiO_2 powders were added to the $MgNb_2O_6$ powders synthesized at 1000°C. The mixed powders were calcined at 850°C for 8 h. The PMNZT calcined powders with the addition of CuO as a sintering aid were pressed into discs and sintered at temperatures from 950 to 1200°C for 4 h in a $PbZrO_3$ atmosphere.

The microstructure was observed with scanning electron microscopy (SEM) and crystal structure was determined using X-ray diffraction (XRD). For electrical characterization, samples were polished to a 1 mm thickness and painted

*Corresponding author: minsoo@keri.re.kr

with fired-on silver paste on the sample surfaces. The samples were poled at 150°C for 30 min under an electric field of 3 kV/mm in silicone oil. The piezoelectric constant (d_{33}) was measured by a quasi-static meter of Berlincourt type. The electromechanical coupling factor (k_P) was determined from resonance-antiresonance methods using an impedance analyzer.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the PMNZT samples with various amounts of CuO addition sintered at 1050°C. A single PMNZT phase with the perovskite structure formed but other phases could not be detected in all of the samples.

The densities as a function of sintering temperature for PMNZT ceramics with various CuO additions are shown in Fig. 2. The density of the samples without CuO increased as the sintering temperature increased and the samples sintered at 1200°C showed the maximum value of 7.75 g/cm^3. The samples could not be fully densified at sintering temperatures lower than 1050°C. However, addition of CuO markedly improved the sinterability of PMNZT ceramics and caused an increase in the density. As the CuO was added to 0.05 wt%, densification behavior was similar to that of the samples without CuO but the values of the density increased. As the CuO was added to 0.1, the density of samples sintered at 1050°C showed the maximum value of 7.78 g/cm^3 and then decreased. The samples with 0.2 wt% CuO showed similar behavior to that of 0.1 wt% CuO. The density of the samples with 0.3 wt% CuO showed the maximum value of 7.77 g/cm^3 at 950°C and then decreased as the sintering temperature increased. The addition of CuO apparently lowers the sintering temperature of the PMNZT ceramics. The sinterability of the ceramics with various amounts of CuO addi-

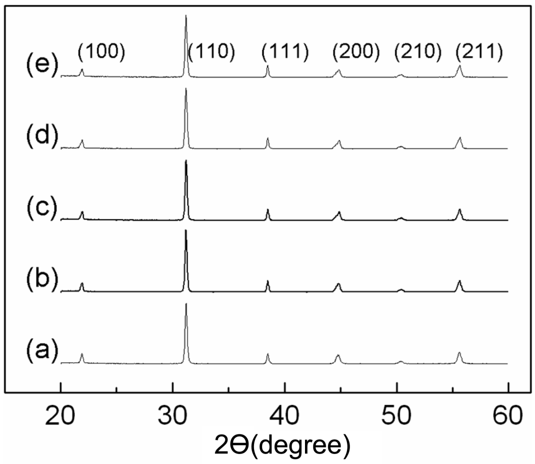

Fig. 1. X-ray diffraction patterns of the PMNZT ceramics with (a) 0, (b) 0.05 (c) 0.1 (d) 0.2 (e) 0.3 wt% of CuO additions sintered at 1050°C.

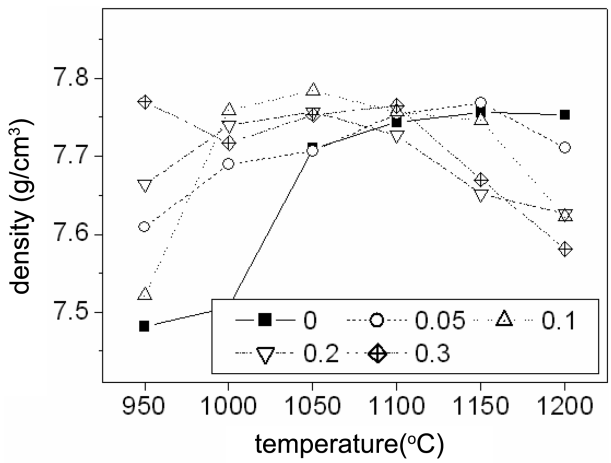

Fig. 2. Densities as a function of sintering temperature for PMNZT ceramics with various CuO additions.

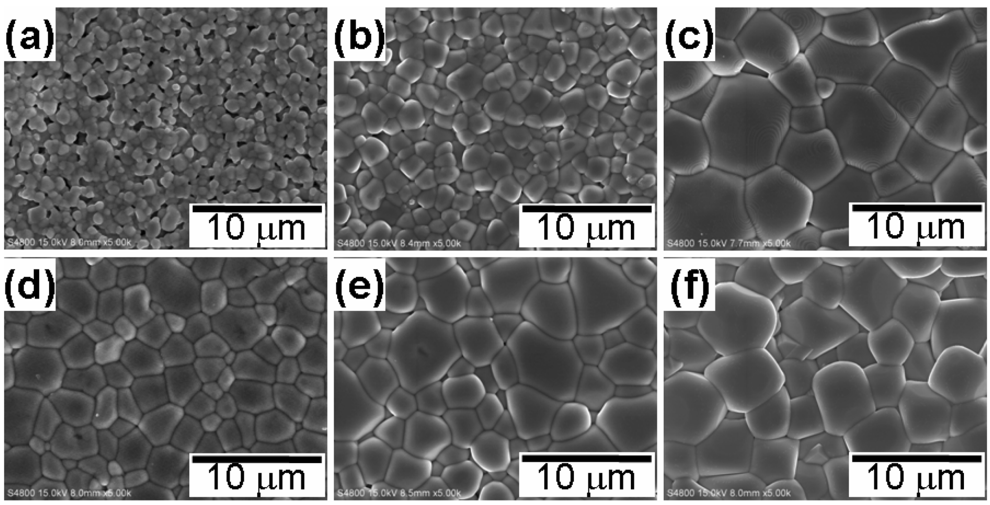

Fig. 3. SEM micrographs of thermally etched surfaces of the pure PMNZT ceramics sintered at (a) 950, (b) 1050, (c) 1200°C, and samples with the addition of 0.1 wt% CuO sintered at (d) 950, (e) 1050, (f) 1200°C for 4 h in air.

tive was examined to determine the optimum amount of addition. It was found that the amount of sintering aids required to induce the sintering at low temperatures of less than 1050°C was higher than 0.1 wt%.

Figure 3 shows SEM micrographs of the thermally etched surfaces of the pure PMNZT ceramics sintered for 4 h in air at (a) 950, (b) 1050, (c) 1200°C, and the samples with the addition of 0.1 wt% CuO sintered at (d) 950, (e) 1050, (f) 1200°C, respectively. The grain size of the pure samples increased with increase in sintering temperature (Fig. 3(a), (b) and (c)). In the case of samples with CuO addition, the grain size increased gradually as sintering temperature increased, and at 1200°C, the grain size was similar to that of the pure sample (Fig. 3(f)). When the samples added 0.1 wt% CuO, the sinterability at low temperature (950°C) was enhanced and the grain size increased dramatically, corresponding to that of the 1050°C - sintered samples without CuO (Fig. 3(b) and (d)). Therefore, the grain growth was also promoted by the addition of CuO. However, all of the samples with the addition of CuO (0, 0.05, 0.1, 0.2, 0.3 wt%) sintered at 1200°C indicated that their grain sizes were similar although the densities were different. Ahn *et al.* [19] have reported that the grain growth and sinterability with the addition of CuO were attributable to liquid phase sintering in the $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ system. The liquid phase formed by CuO addition was volatilized at high temperature and the effect of CuO was dominant at lower sintering temperature.

The electrical properties of the ceramics were evaluated as a function of sintering temperature. Figure 4 shows the piezoelectric coefficient (d_{33}), planar mode electromechanical coupling coefficient (k_P), and dielectric constant (ε_r), of the pure and CuO added samples sintered for 4 h in air at various temperatures. It is clear that, d_{33}, k_P and ε_r possess a peak with increasing sintering temperature. The d_{33} values of the samples without CuO increased as the sintering temperature increased and the samples that were sintered at 1200°C showed the maximum value of 622 pC/N. As 0.05 wt% CuO was added, the d_{33} values increased. When the sintering temperature for 0.1 wt% CuO added samples increased to 1050°C, the piezoelectric property started to decrease. The samples with 0.2 wt% CuO showed the maximum d_{33} value at 1000°C and then dramatically decreased as the sintering temperature increased. The samples with CuO addition showed relatively high d_{33} constants at low sintering temperature. These results are coincident with the trends of density and grain size according to the amount of CuO addition as shown in Fig. 2 and 3. The samples showed their peak d_{33} values at their corresponding sintering temperatures. The sintering temperature of the maximum d_{33} value was the same from the point where the peak density was achieved.

Addition of CuO markedly increased the electromechanical coupling factors of the samples as shown in Fig. 4. The samples with 0.1 wt% CuO showed relatively high and steady k_P constants of about 0.70-0.72 as the sintering temperature was increased from 1000 up to 1150°C, and turned to an apparent drop when sintered above 1150°C, which is consistent with the decrease in density and piezoelectric property as shown in Fig. 2 and 4. For all of the samples, the k_P curve showed similar behavior to piezoelectric properties. When the samples with a composition of 0.1 wt% CuO addition sintered at 1050°C for 4 h, k_P and d_{33} were found to reach the highest values of 0.72 and 663 pC/N, respectively. In the case of the dielectric properties of the samples, they still showed a similar tendency to those in their electrical properties.

These results indicate that electrical properties can be improved by control of microstructures, including grain growth and densities. Consequently, CuO addition to PMNZT ceramics could lead to low temperature sintering, and at the same time improve piezoelectric properties.

4. CONCLUSIONS

The effect of CuO additions on the microstructures and electromechanical properties of PMNZT ceramics was investigated. The addition of CuO improved the sinterability of the samples and caused a decrease in the sintering temperature. When samples of high density with a composition of 0.1 wt% CuO added were sintered at 1050°C for 4 h, electro-

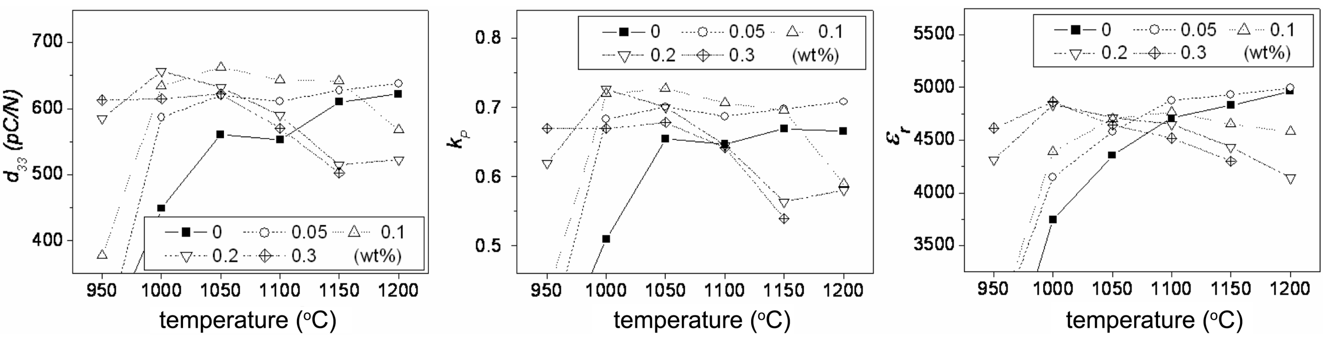

Fig. 4. Piezoelectric coefficients (d_{33}), planar mode electromechanical coupling coefficients (k_P), and dielectric constants (ε_r) of pure and CuO added PMNZT ceramics sintered for 4 h in air at various temperatures.

mechanical coupling factor and piezoelectric coefficient were found to reach the highest values of 0.72 and 663 pC/N, respectively. These results show that the piezoelectric properties of PMNZT samples can be improved by controlling the microstructures; this system is potentially a good candidate as a multilayer piezoelectric device for a wide range of electro-mechanical transducer applications.

ACKNOWLEDGMENT

This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Ministry of Knowledge Economy, Republic of Korea.

REFERENCES

1. B. Jaffe, R. S. Roth, and S. Marzullo, *J. Appl. Phys.* **25**, 809 (1954).
2. B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*, p.135-160, Academic Press, New York (1971).
3. H.-J. Noh and S.-G. Lee, *Electron Mater. Lett.* **3**, 191 (2007).
4. S. F. Wang and W. Huebner, *J. Am. Ceram. Soc.* **74,** 1349 (1991).
5. S. F. Wang, J. P. Dougherty, W. Huebner, and J. G. Pepin, *J. Am. Ceram. Soc.* **77**, 3051 (1994).
6. K. Shiratsuyu, K. Hayashi, A. Ando, and Y. Sakabe, *Jpn. J. Appl. Phys.* **39**, 5609 (2000).
7. G. H. Haertling and C. E. Land, *J. Am. Ceram. Soc.* **54**, 11 (1971).
8. M. Murata, K. Wakino. K. Tanaka, and Y. Hamakawa, *Mater. Res. Bull.* **11**, 323 (1976).
9. T. Ikeda and T. Okano, *Jpn, J. Appl. Phys.* **2**, 63 (1963).
10. S. Kaneko, D. Dong, and K. Murakami, *J. Am. Ceram. Soc.* **81**, 1013 (1998).
11. X. Wang, K. Murakami, and S. Kaneko, *Jpn. J. Appl. Phys.* **39**, 5556 (2000).
12. C.-W. Ahn, H.-C. Song, S.-H. Park, S. Nahm, K. Uchino, S. Priya, H.-G. Lee, and N.-K. Kang, *Jpn. J. Appl. Phys.* **44**, 1314 (2005).
13. T. Hayashi, T. Inoue, and Y. Akiyama, *Jpn. J. Appl. Phys.* **38**, 5549 (1999).
14. L. Wu and C. H. Wang, *Jpn. J. Appl. Phys.* **32**, 2757 (1993).
15. G. Zhilun, L. Longtu, G. Suhua, and Z. Xiaowen, *J. Am. Ceram. Soc.* **72**, 486 (1989).
16. D. E. Whittmer and R. C. Buchauan, *J. Am. Ceram. Soc.* **64**, 485 (1981).
17. H. Ouchi, K. Nagano, and S. Hayakawa, *J. Am. Ceram. Soc.* **48**, 630 (1965).
18. S. L. Swartz and T. R. Shrout, *Mater. Res. Bull.* **17**, 1245 (1982).
19. C. W. Ahn, S. Nahm, J. Ryu, K. Uchino, S.-J. Yoon, S.-J. Jung, and J.-S. Song, *Jpn. J. Appl. Phys.* **43**, 205 (2004).